Chapter 5 The Second Law of Thermodynamics (continued)

Second Law of Thermodynamics

Alternative statements of the second law,

<u>Clausius Statement</u> of the Second Law

It is impossible for any system to operate in such a way that the sole result would be an energy transfer by heat from a cooler to a hotter body.



Second Law of Thermodynamics

Alternative statements of the second law,

<u>Kelvin-Planck Statement</u> of the Second Law

It is impossible for any system to operate in a thermodynamic cycle and deliver a net amount of energy by work to its surroundings while receiving energy by heat transfer from a single thermal reservoir.



Aspects of the Second Law of Thermodynamics

From conservation of mass and energy principles, (i.e. 1st Law of Thermodynamics)

mass and energy cannot be created or destroyed.

► For a process, conservation of mass and energy principles indicate the disposition of mass and energy but do not infer whether the process can actually occur.

The second law of thermodynamics provides the guiding principle for whether a process can occur.

<u>Second Law of Thermodynamics</u> <u>Alternative Statements</u>

There is no simple statement that captures all aspects of the second law. Several alternative formulations of the second law are found in the technical literature. Three prominent ones are:

Clausius Statement

- Kelvin-Planck Statement
- Entropy Statement

It is impossible for any system to operate in a way that entropy is destroyed.

Irreversible and Reversible Processes

During a process (i.e. a change from State A to State B) of a system, **irreversibilities** may be present:

- within the system, or
- with its surroundings (usually the immediate surroundings), or
- ► both.

Applications to Power Cycles Interacting with Two Thermal Reservoirs

For a system undergoing a power cycle while communicating thermally with *two* thermal reservoirs, a hot reservoir and a cold reservoir, the thermal efficiency of any such cycle is



By applying the **Kelvin-Planck statement** of the **second law**, Eq. 5.3, three conclusions can be drawn:



- The value of the thermal efficiency must be less than 100%.
- 2. The thermal efficiency of an irreversible power cycle is **always less than** the thermal efficiency of a reversible power cycle for the same two thermal reservoirs, and
- 3. All reversible power cycles operating between the same two thermal reservoirs have the **same thermal efficiency**.

Applications to Refrigeration and Heat Pump Cycles Interacting with *Two* Thermal Reservoirs

For a system undergoing a refrigeration cycle or heat pump cycle while communicating thermally with *two* thermal reservoirs, a hot reservoir and a cold reservoir, the coefficient of performance

Hot $Q_H =$ $Q_C + W_{cycle}$ Boundary Cold reservoir Q_C Q_C $W_{cycle} = Q_H - Q_C$ an

the coefficient of performance for the refrigeration cycle is

$$\beta = \frac{Q_{\rm C}}{W_{\rm cycle}} = \frac{Q_{\rm C}}{Q_{\rm H} - Q_{\rm C}} \quad \text{(Eq. 5.5)}$$

and for the heat pump cycle is

$$\gamma = \frac{Q_{\rm H}}{W_{\rm cycle}} = \frac{Q_{\rm H}}{Q_{\rm H} - Q_{\rm C}}$$



By applying the **Kelvin-Planck statement** of the second law, Eq. 5.3, three conclusions can be drawn:

- 1. For a refrigeration effect to occur a net work input W_{cycle} is required. Accordingly, the coefficient of performance must be finite in value.
- 2. The coefficient of performance of an irreversible refrigeration cycle is **always less than** the coefficient of performance of a reversible refrigeration cycle when each operates between the same two thermal reservoirs.
- 3. All reversible refrigeration cycles operating between the same two thermal reservoirs have the same coefficient of performance.

Kelvin Temperature Scale

Consider systems undergoing a power cycle and a refrigeration or heat pump cycle, each while exchanging energy by heat transfer with hot and cold reservoirs:





The Kelvin temperature is defined so that

$$\left(\frac{Q_{\rm C}}{Q_{\rm H}}\right)_{\rm rev}_{\rm cycle} = \frac{T_{\rm C}}{T_{\rm H}} \qquad (Eq. 5.7)$$

Maximum Performance Measures for Cycles Operating between Two Thermal Reservoirs

It follows that the **maximum theoretical** thermal efficiency and coefficients of performance in these cases are **achieved only by reversible cycles**. Using Eq. 5.7 in Eqs. 5.4, 5.5, and 5.6, we get respectively:

Power Cycle: $\eta_{max} = 1 - \frac{T_C}{T_H}$ (Eq. 5.9)Refrigeration Cycle: $\beta_{max} = \frac{T_C}{T_H - T_C}$ (Eq. 5.10)Heat Pump Cycle: $\gamma_{max} = \frac{T_H}{T_H - T_C}$ (Eq. 5.11)

where $T_{\rm H}$ and $T_{\rm C}$ must be on the Kelvin or Rankine scale.

Example: Power Cycle Analysis

A system undergoes a power cycle while receiving 1000 kJ by heat transfer from a thermal reservoir at a temperature of 500 K and discharging 600 kJ by heat transfer to a thermal reservoir at (a) 200 K, (b) 300 K, (c) 400 K. For each case, **determine** whether the cycle operates *irreversibly*, operates *reversibly*, or is *impossible*.



Solution: To determine the nature of the cycle, **compare** actual cycle performance (η) to maximum theoretical cycle performance (η_{max}) calculated from Eq. 5.9

Example: Power Cycle Analysis

Actual Performance: Calculate η using

the heat transfers:

$$\eta = 1 - \frac{Q_{\rm C}}{Q_{\rm H}} = 1 - \frac{600 \,\text{kJ}}{1000 \,\text{kJ}} = 0.4$$



Maximum Theoretical Performance:Calculate η_{max} from Eq. 5.9 and compareto η : $\underline{\eta}$ $\underline{\eta}$

(a)
$$\eta_{\text{max}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}} = 1 - \frac{200 \text{ K}}{500 \text{ K}} = 0.6$$

(b) $\eta_{\text{max}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}} = 1 - \frac{300 \text{ K}}{500 \text{ K}} = 0.4$
(c) $0.4 < 0.6 \rightarrow \text{Irreversibly}$
(c) $0.4 = 0.4 \rightarrow \text{Reversibly}$

(c)
$$\eta_{\text{max}} = 1 - \frac{T_{\text{C}}}{T_{\text{H}}} = 1 - \frac{400 \text{ K}}{500 \text{ K}} = 0.2$$
 0.4 > 0.2 → Impossible

Carnot Cycle

- The Carnot cycle provides a specific example of a reversible cycle that operates between two thermal reservoirs. Other examples are provided in Chapter 9: the Ericsson and Stirling cycles.
- In a Carnot cycle, the system executing the cycle undergoes a series of four internally reversible processes: two adiabatic processes alternated with two isothermal processes.

Carnot Power Cycles

The *p*-*v* diagram and schematic of a gas in a piston-cylinder assembly executing a Carnot cycle are shown below:



Carnot Power Cycles

The *p*-*v* diagram and schematic of water executing a Carnot cycle through four interconnected components are shown below:



In each of these cases the thermal efficiency is given by

$$\eta_{\rm max} = 1 - \frac{T_{\rm C}}{T_{\rm H}}$$
 (Eq. 5.9)

Carnot Refrigeration and Heat Pump Cycles

- If a Carnot power cycle is operated in the opposite direction, the magnitudes of all energy transfers remain the same but the energy transfers are oppositely directed.
- Such a cycle may be regarded as a Carnot refrigeration or heat pump cycle for which the coefficient of performance is given, respectively, by

Carnot Refrigeration Cycle:

$$\beta_{\rm max} = \frac{T_{\rm C}}{T_{\rm H} - T_{\rm C}}$$
 (Eq. 5.10)

Carnot Heat Pump Cycle:

$$\gamma_{\rm max} = \frac{T_{\rm H}}{T_{\rm H} - T_{\rm C}}$$

(Eq. 5.11)

Clausius Inequality

- The Clausius inequality considered next provides the basis for developing the entropy concept in Chapter 6.
- The Clausius inequality is applicable to any cycle without regard for the body, or bodies, from which the system undergoing a cycle receives energy by heat transfer or to which the system rejects energy by heat transfer. Such bodies need not be thermal reservoirs.

Clausius Inequality

The Clausius inequality is developed from the Kelvin-Planck statement of the second law and can be expressed as:

$$\oint \left(\frac{\delta Q}{T}\right)_{\rm b} = -\sigma_{\rm cycle} \qquad (Eq. 5.13)$$

where

- indicates integral is to be performed over all parts of the boundary and over the entire cycle.
- **b** subscript indicates integrand is evaluated at the boundary of the system executing the cycle.

Clausius Inequality

The Clausius inequality is developed from the Kelvin-Planck statement of the second law and can be expressed as:

$$\oint \left(\frac{\delta Q}{T}\right)_{\rm b} = -\sigma_{\rm cycle} \qquad (Eq. 5.13)$$

The nature of the cycle executed is indicated by the value of σ_{cycle} :

 $\begin{aligned} \sigma_{\text{cycle}} &= 0 & \text{no irreversibilities present within the system} \\ \sigma_{\text{cycle}} &> 0 & \text{irreversibilities present within the system} \\ \sigma_{\text{cycle}} &< 0 & \text{impossible} \end{aligned}$



Example: Use of Clausius Inequality

A system undergoes a cycle while receiving 1000 kJ by heat transfer at a temperature of 500 K and discharging 600 kJ by heat transfer at (a) 200 K, (b) 300 K, (c) 400 K. Using Eqs. 5.13 and 5.14, what is the nature of the cycle in each of these cases?

Solution: To determine the nature of the cycle, perform the cyclic integral of Eq. 5.13 to each case and apply Eq. 5.14 to draw a conclusion about the nature of each cycle.

Example: Use of Clausius Inequality

Applying Eq. 5.13 to each cycle:
$$\oint \left(\frac{\delta Q}{T}\right)_{b} = \frac{Q_{in}}{T_{H}} - \frac{Q_{out}}{T_{C}} = -\sigma_{cycle}$$
(a) $-\sigma_{cycle} = \frac{1000 \text{ kJ}}{500 \text{ K}} - \frac{600 \text{ kJ}}{200 \text{ K}} = -1 \text{ kJ/K} \rightarrow \sigma_{cycle} = +1 \text{ kJ/K} > 0$
Irreversibilities present within system
(b) $-\sigma_{cycle} = \frac{1000 \text{ kJ}}{500 \text{ K}} - \frac{600 \text{ kJ}}{300 \text{ K}} = 0 \text{ kJ/K} \rightarrow \sigma_{cycle} = 0 \text{ kJ/K} = 0$
No irreversibilities present within system
(c) $-\sigma_{cycle} = \frac{1000 \text{ kJ}}{500 \text{ K}} - \frac{600 \text{ kJ}}{400 \text{ K}} = 0.5 \text{ kJ/K} \rightarrow \sigma_{cycle} = -0.5 \text{ kJ/K} < 0$
Impossible