Chapter 5

The Second Law of Thermodynamics

Learning Outcomes

- ►Demonstrate understanding of key concepts related to the second law of thermodynamics, including
  - ►alternative statements of the second law,
  - ►the internally reversible process, and
  - ►the Kelvin temperature scale.
- ►List several important irreversibilities.

Learning Outcomes, cont.

- Assess
  - the performance of power cycles and refrigeration and heat pump cycles using, as appropriate, the corollaries of Secs. 5.6.2 and 5.7.2, together with Eqs. 5.9-5.11.
- Describe the Carnot cycle.
- Interpret the Clausius inequality as expressed by Eq. 5.13.

Aspects of the Second Law of Thermodynamics

- ►From conservation of mass and energy principles,
  - ► 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.

Aspects of the
Second Law of Thermodynamics

The second law of thermodynamics has many aspects, which at first may appear different in kind from those of conservation of mass and energy principles. Among these aspects are:

- ►predicting the **direction of processes**.
- ►establishing **conditions for equilibrium**.
- ►determining the **best *theoretical* performance** of cycles, engines, and other devices.
- ►evaluating quantitatively the **factors** that **preclude attainment of the best theoretical performance level**.

Aspects of the Second Law of Thermodynamics

Other aspects of the second law include:

- ►defining a **temperature scale** independent of the properties of any thermometric substance.
- ►developing means for **evaluating properties** such as u and h in terms of properties that are more readily obtained experimentally.

Scientists and engineers have found additional uses of the second law and deductions from it. It also has been used in philosophy, economics, and other disciplines far removed from engineering thermodynamics.

Second Law of Thermodynamics Alternative Statements

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:

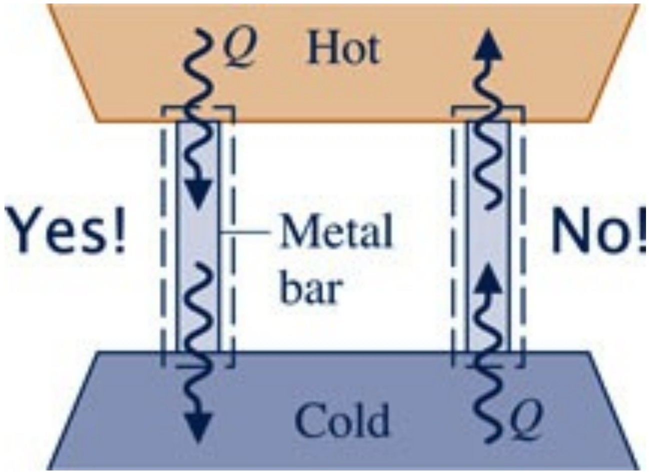
- ►Clausius Statement
- ►Kelvin-Planck Statement
- ►Entropy Statement

Second Law of Thermodynamics Alternative Statements

- The focus of **Chapter 5** is on the **Clausius** and **Kelvin-Planck statements**.
- The **Entropy statement** is developed and applied in **Chapter 6**.
- Like every physical *law*, the **basis of the second law of thermodynamics is experimental evidence**. While the three forms given are not directly demonstrable in the laboratory, deductions from them can be verified experimentally, and this infers the validity of the second law statements.

Clausius Statement 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.

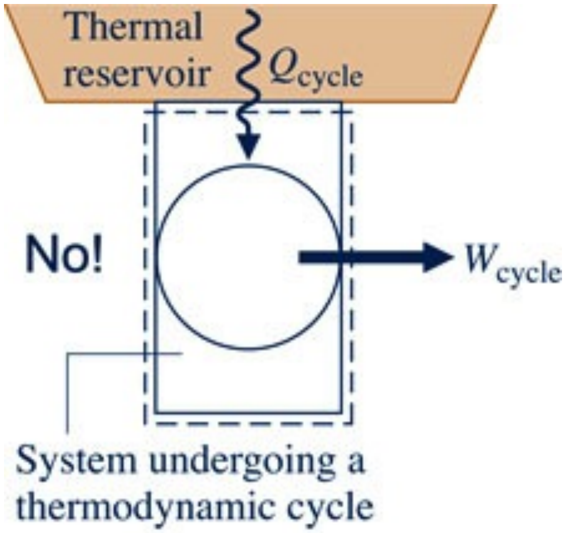


Thermal Reservoir

- A **thermal reservoir** is a system that always remains at constant temperature even though energy is added or removed by heat transfer.
- Such a system is approximated by the earth’s atmosphere, lakes and oceans, and a large block of a solid such as copper.

Kelvin-Planck Statement 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.



Entropy Statement of the Second Law

- ► Mass and energy are familiar examples of extensive properties used in thermodynamics.
- ► Entropy is another important extensive property. How entropy is evaluated and applied is detailed in Chapter 6.
- ► Unlike mass and energy, which are conserved, entropy is produced within systems whenever non-idealities such as friction are present.
- ► **The Entropy Statement is**:

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

Irreversibilities

- One of the important uses of the second law of thermodynamics in engineering is to determine the *best theoretical performance* of systems.
- By comparing actual performance with best theoretical performance, insights often can be had about the potential for improved performance.
- Best theoretical performance is evaluated in terms of *idealized* processes.
- Actual processes are distinguishable from such idealized processes by the presence of non-idealities – called **irreversibilities**.

Irreversibilities Commonly Encountered in Engineering Practice

- ►Heat transfer through a finite temperature difference
- ►Unrestrained expansion of a gas or liquid to a lower pressure
- ►Spontaneous chemical reaction
- ►Spontaneous mixing of matter at different compositions or states
- ►Friction – sliding friction as well as friction in the flow of fluids

Irreversibilities Commonly Encountered in Engineering Practice

- ►Electric current flow through a resistance
- ►Magnetization or polarization with hysteresis
- ►Inelastic deformation

All actual processes involve effects such as those listed, including naturally occurring processes and ones involving devices we construct – from the simplest mechanisms to the largest industrial plants.

Irreversible and Reversible Processes

During a process of a system, **irreversibilities** may be present:

► within the system, or

► within its surroundings (usually the immediate surroundings), or

► within both the system and its surroundings.

Irreversible and Reversible Processes

- A process is ***irreversible*** when irreversibilities are present within the system and/or its surroundings.

  All actual processes are irreversible.

- A process is ***reversible*** when no irreversibilities are present within the system and its surroundings.

  This type of process is fully idealized.

Irreversible and Reversible Processes

- ►A process is ***internally reversible*** when no irreversibilities are present within the system. Irreversibilities may be present within the surroundings, however.

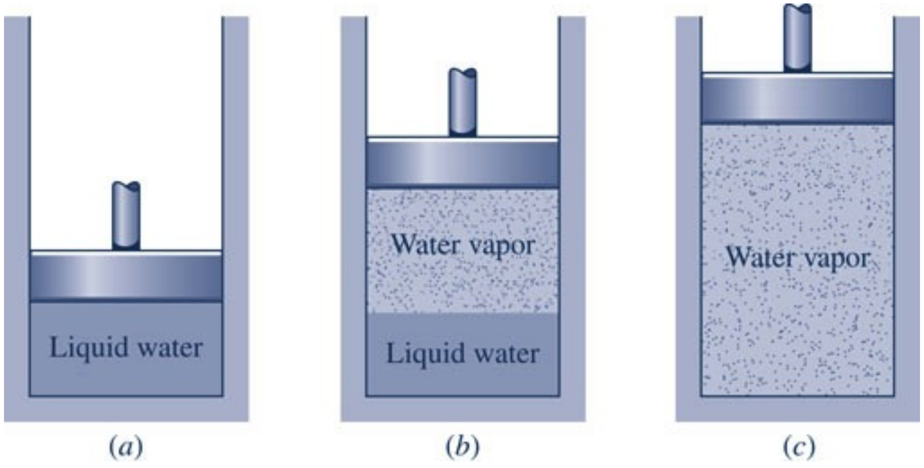
  An internally reversible process is a quasiequilibrium process (see Sec. 2.2.5).

Example: Internally Reversible Process

Water contained within a piston-cylinder changes phase from saturated liquid to saturated vapor at 100°C. As the water evaporates, it passes through a sequence of equilibrium states while there is heat transfer to the water from hot gases at 500°C.

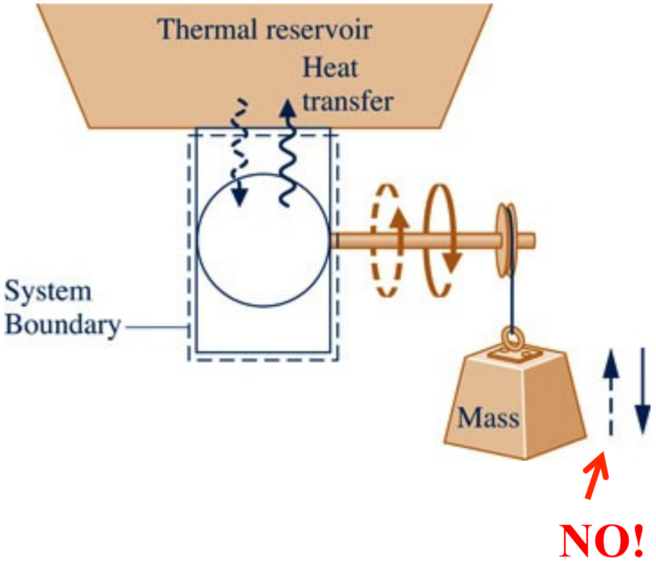
►For a system enclosing the water there are **no *internal* irreversibilities**, but

►Such spontaneous heat transfer is an irreversibility in its surroundings: an ***external* irreversibility**.



Analytical Form of the Kelvin-Planck Statement

For any system undergoing a thermodynamic cycle while exchanging energy by heat transfer with a *single* thermal reservoir, the net work, W_{cycle}, can be only negative or zero – never positive:

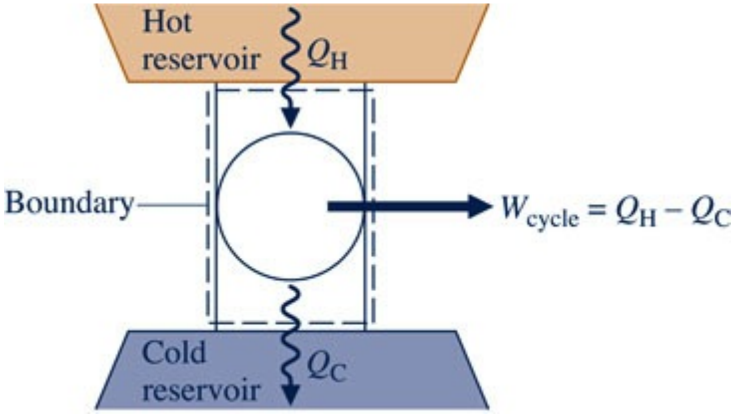


$$W_{\text{cycle}} \leq 0 \begin{cases} < 0: & \text{Internal irreversibilities present} \\ = 0: & \text{No internal irreversibilities} \end{cases} \quad \left(\begin{array}{c}\text{single}\\ \text{reservoir}\end{array}\right)$$

(Eq. 5.3)

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**



$$\eta = \frac{W_{\text{cycle}}}{Q_H} = 1 - \frac{Q_C}{Q_H} \quad \textbf{(Eq. 5.4)}$$

Applications to Power Cycles Interacting with *Two* Thermal Reservoirs

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

1. The value of the **thermal efficiency must be less than 100%**. Only a portion of the heat transfer Q_H can be obtained as work and the remainder Q_C is discharged by heat transfer to the cold reservoir.

Two other conclusions, called the *Carnot corollaries*, are:

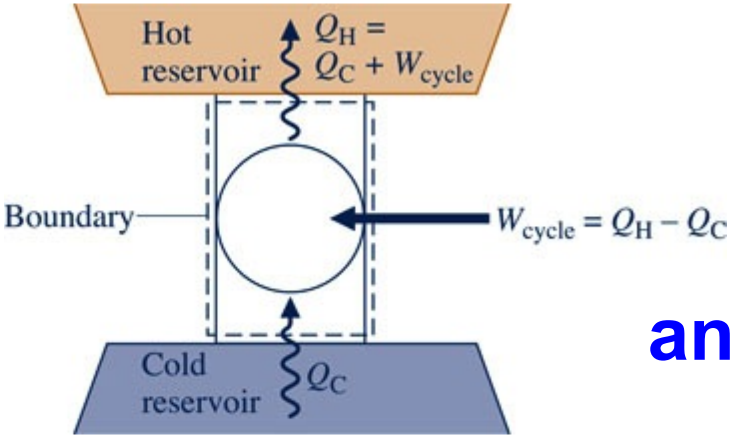
Carnot Corollaries

1. The thermal efficiency of an irreversible power cycle is **always less than** the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs.
2. All reversible power cycles operating between the same two thermal reservoirs have the **same thermal efficiency**.

A cycle is considered ***reversible*** when there are no irreversibilities within the system as it undergoes the cycle and heat transfers between the system and reservoirs occur reversibly.

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 for the refrigeration cycle is

$$\beta = \frac{Q_C}{W_{cycle}} = \frac{Q_C}{Q_H - Q_C}$$

(Eq. 5.5)

and for the heat pump cycle is

$$\gamma = \frac{Q_H}{W_{cycle}} = \frac{Q_H}{Q_H - Q_C}$$

(Eq. 5.6)

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

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**.

Two other conclusions are:

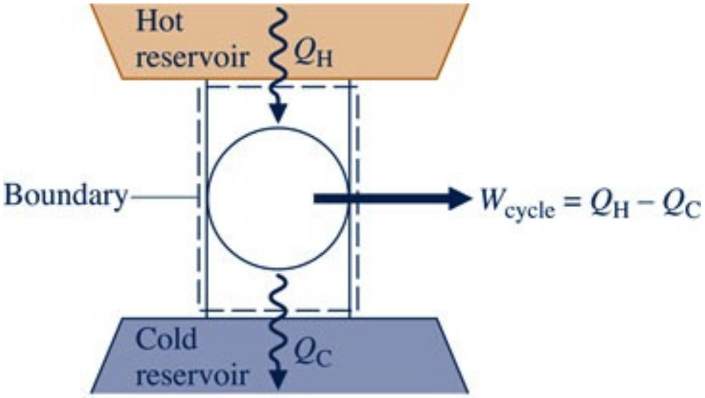
Applications to Refrigeration and Heat Pump Cycles Interacting with *Two* Thermal Reservoirs

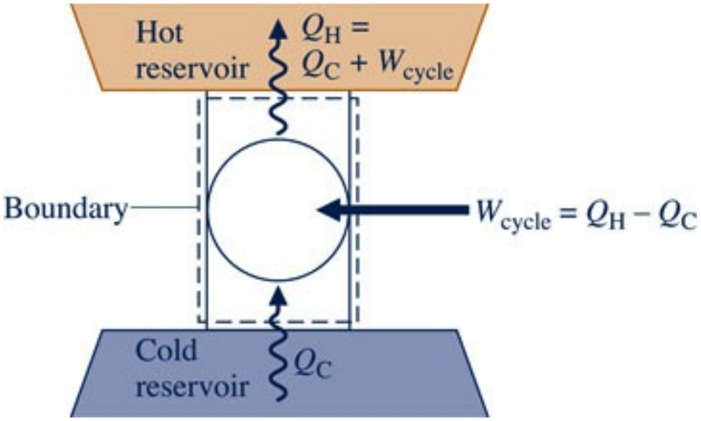
2. The coefficient of performance of an irreversible refrigeration cycle is **always less than** the coefficient of performance of a reversible refrigeration cycle when each operates between the same two thermal reservoirs.
3. All reversible refrigeration cycles operating between the same two thermal reservoirs have the **same coefficient of performance**.

All three conclusions also apply to a system undergoing a heat pump cycle between hot and cold reservoirs.

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

$$\left(\frac{Q_C}{Q_H}\right)_{\substack{\text{rev}\\ \text{cycle}}} = \frac{T_C}{T_H}$$

(Eq. 5.7)

Kelvin Temperature Scale

- ►In words, Eq. 5.7 states: When cycles are ***reversible***, and only then, the ratio of the heat transfers equals a ratio of temperatures on the Kelvin scale, where T_H is the temperature of the hot reservoir and T_C is the temperature of the hot reservoir.
- ►As temperatures on the Rankine scale differ from Kelvin temperatures only by the factor 1.8: $T(^{o}\mathrm{R})=1.8T(\mathrm{K})$, the T's in Eq. 5.7 may be on either scale of temperature. Equation 5.7 is not valid for temperatures in ^{o}C or ^{o}F, for these do not differ from Kelvin temperatures by only a factor:

$$\mathbf{T(^{o}C) = T(K) - 273.15}$$

$$\mathbf{T(^{o}F) = T(R) - 459.67}$$

Maximum Performance Measures for Cycles Operating between Two Thermal Reservoirs

Previous deductions from the Kelvin-Planck statement of the second law include:

1. The thermal efficiency of an irreversible power cycle is **always less than** the thermal efficiency of a reversible power cycle when each operates between the same two thermal reservoirs.
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. The coefficient of performance of an irreversible heat pump cycle is **always less than** the coefficient of performance of a reversible heat pump cycle when each operates between the same two thermal reservoirs.

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:

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

Refrigeration Cycle:

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

Heat Pump Cycle:

$$\gamma_{\max} = \frac{T_{\mathrm{H}}}{T_{\mathrm{H}} - T_{\mathrm{C}}} \qquad \textbf{(Eq. 5.11)}$$

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