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.

<u>Aspects of the</u>
<u>Second Law of Thermodynamics</u>

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:

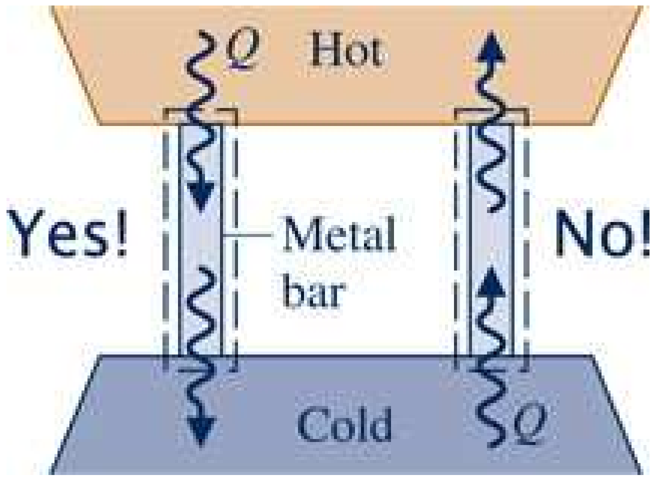
- ►Clausius Statement
- ►Kelvin-Planck Statement
- ►Entropy Statement

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.

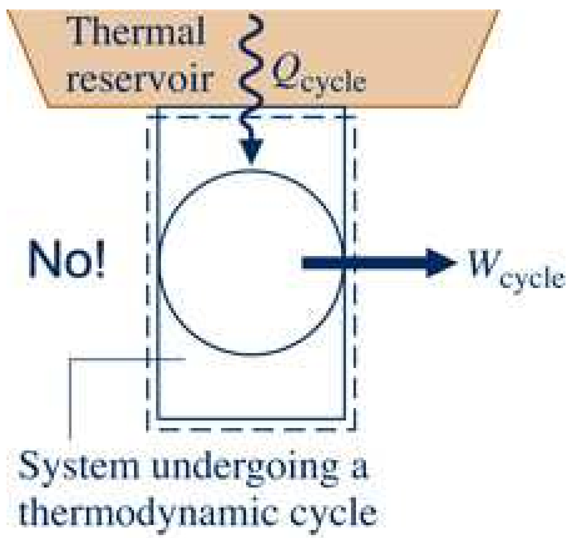


Thermal Reservoir

- 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 evaporates from saturated liquid to saturated vapor at 100^{o}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^{o}C.

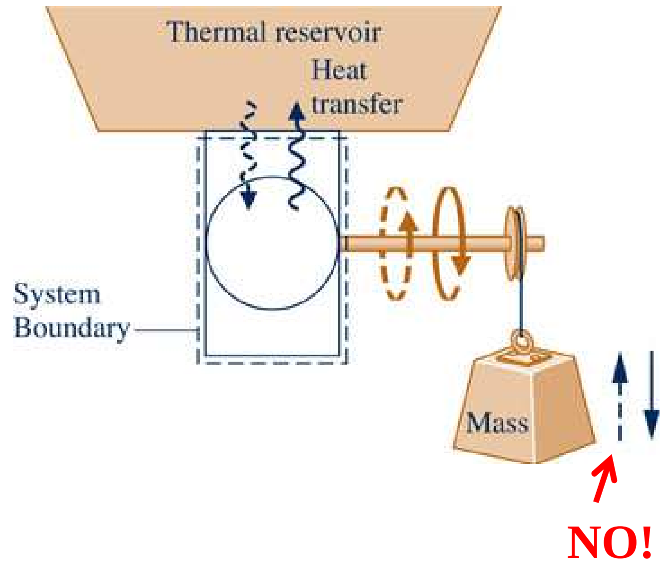
►For a system enclosing the water there are **no *internal* irreversibilities**, but

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

(a) (b) (c)

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**:

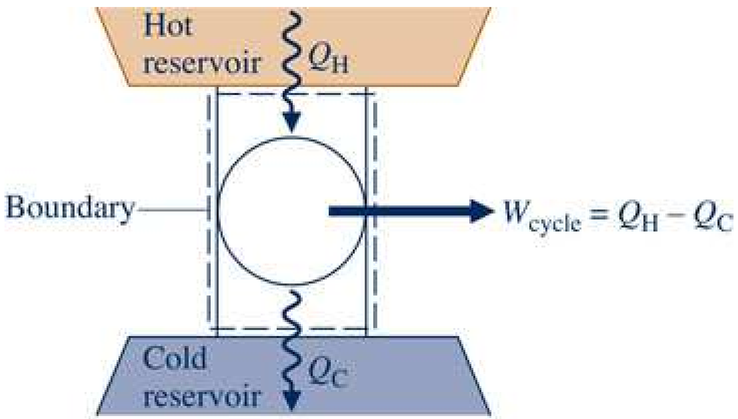


$$W_{cycle} \leq 0 \begin{cases} < 0\text{: Internal irreversibilities present} \\ = 0\text{: No internal irreversibilities} \end{cases} \quad \left(\begin{array}{c}\text{single} \\ \text{reservoir}\end{array}\right)$$

(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**



$$\eta = \frac{W_{cycle}}{Q_H} = 1 - \frac{Q_C}{Q_H}$$ **(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:

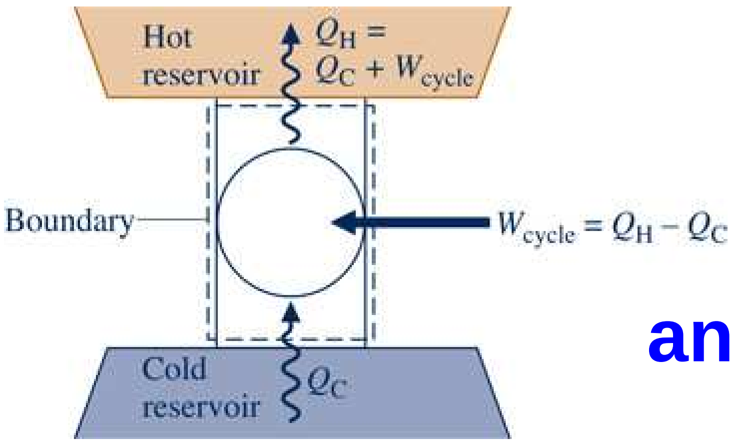
Carnot Corollaries

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:

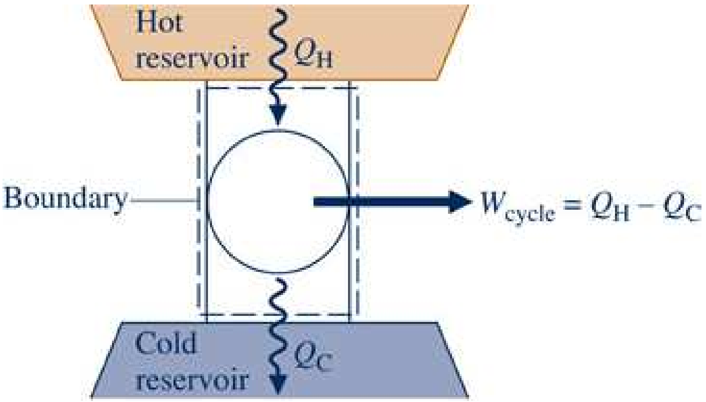
Applications to Refrigeration and Heat Pump Cycles Interacting with *Two* Thermal Reservoirs

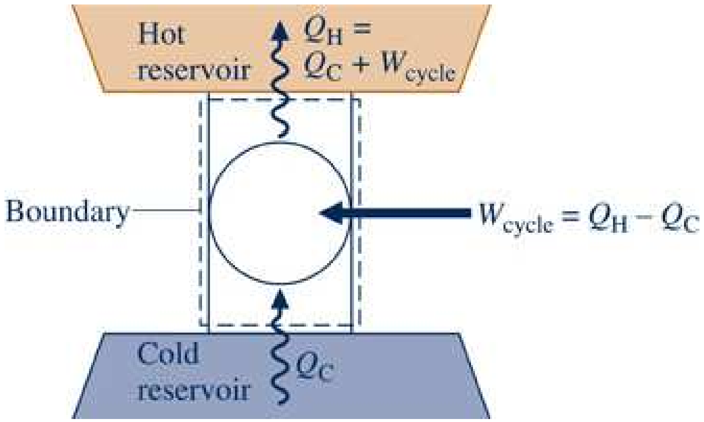
1. The coefficient of performance of an irreversible refrigeration cycle is **always less than** the coefficient of performance of a reversible refrigeration cycle when each operates between the same two thermal reservoirs.
2. All reversible refrigeration cycles operating between the same two thermal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

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

(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.
- Equation 5.7 is not valid for temperatures in ^oC, for these do not differ from Kelvin temperatures by only a factor:

$$T(^oC) = T(K) - 273.15$$

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:

$$\eta_{\max} = 1 - \frac{T_C}{T_H} \quad \text{(Eq. 5.9)}$$

Refrigeration Cycle:

$$\beta_{\max} = \frac{T_C}{T_H - T_C} \quad \text{(Eq. 5.10)}$$

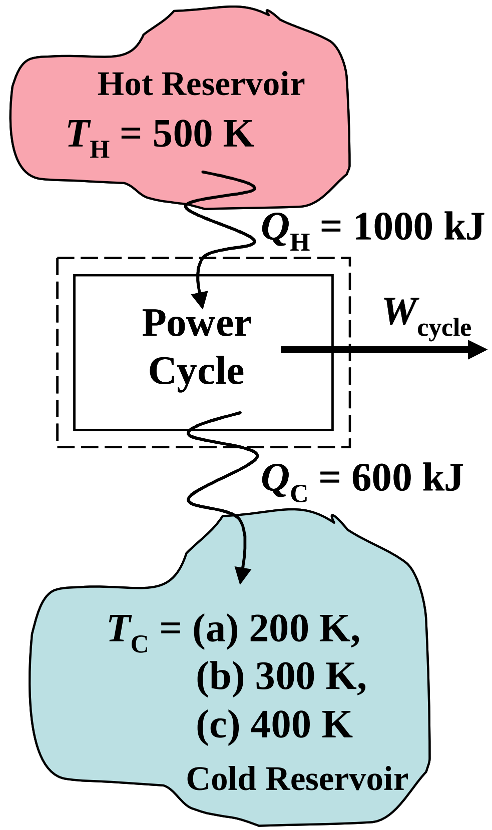
Heat Pump Cycle:

$$\gamma_{\max} = \frac{T_H}{T_H - T_C} \quad \text{(Eq. 5.11)}$$

where T_H and T_C must be on the **Kelvin 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:

$$\eta = 1 - \frac{Q_C}{Q_H} = 1 - \frac{600\ \text{kJ}}{1000\ \text{kJ}} = 0.4$$

Maximum Theoretical Performance: Calculate η_{max} from Eq. 5.9 and compare to η:

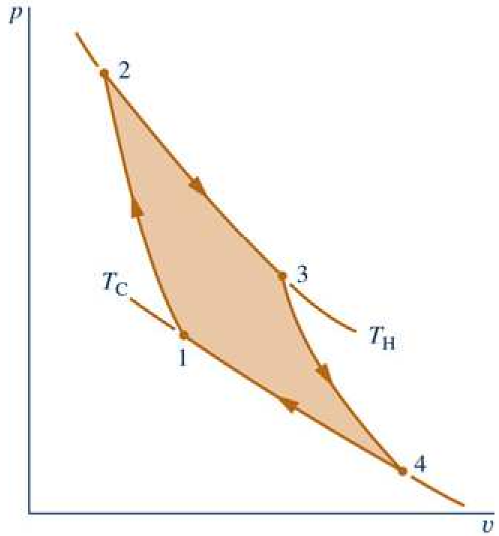
		η		η_{max}		
(a)	$\eta_{max} = 1 - \frac{T_C}{T_H} = 1 - \frac{200\ \text{K}}{500\ \text{K}} = 0.6$	**0.4**	$<$	**0.6**	→	**Irreversibly**
(b)	$\eta_{max} = 1 - \frac{T_C}{T_H} = 1 - \frac{300\ \text{K}}{500\ \text{K}} = 0.4$	**0.4**	$=$	**0.4**	→	**Reversibly**
(c)	$\eta_{max} = 1 - \frac{T_C}{T_H} = 1 - \frac{400\ \text{K}}{500\ \text{K}} = 0.2$	**0.4**	$>$	**0.2**	→	**Impossible**

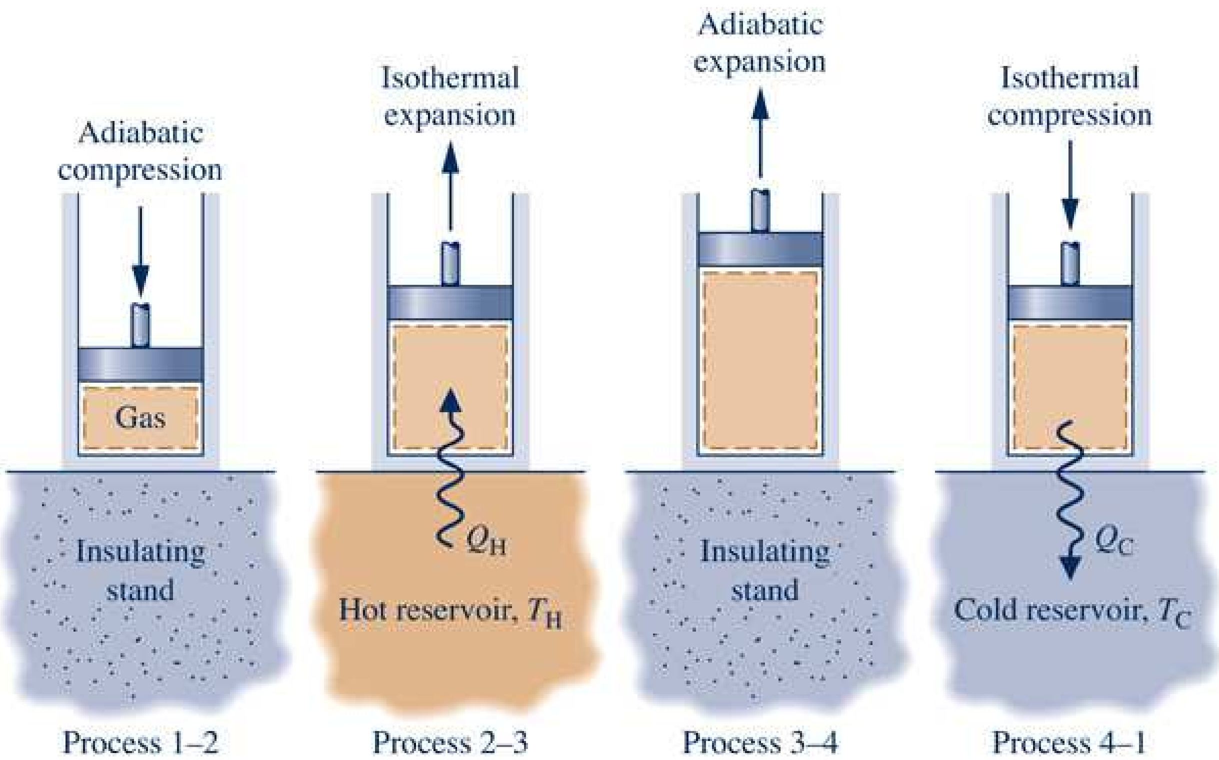
<u>Carnot Cycle</u>

- ►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

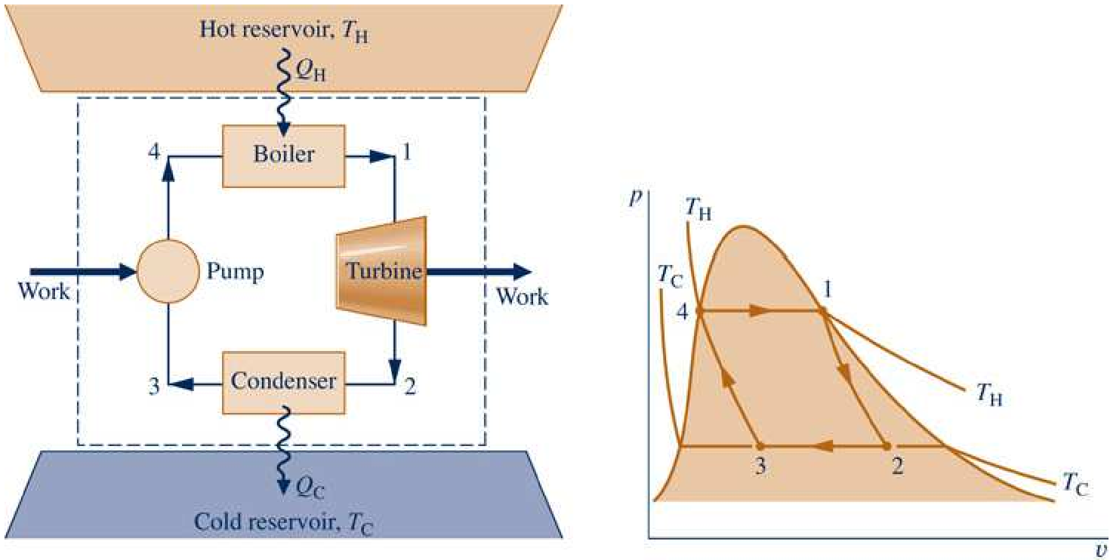
The ***p-v* diagram** and **schematic** of a gas in a piston-cylinder assembly executing a Carnot cycle are shown below:





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

$$\eta_{max} = 1 - \frac{T_C}{T_H}$$

(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:

$$\beta_{\text{max}} = \frac{T_{\text{C}}}{T_{\text{H}} - T_{\text{C}}}$$

(Eq. 5.10)

Carnot Heat Pump Cycle:

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

(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:

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

where

$\oint$ 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:

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

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

$\sigma_{\mathrm{cycle}} = 0$	**no irreversibilities present within the system**	**(Eq. 5.14)**
$\sigma_{\mathrm{cycle}} > 0$	**irreversibilities present within the system**	
$\sigma_{\mathrm{cycle}} < 0$	**impossible**	

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) $-\sigma_{cycle} = \frac{1000\text{ kJ}}{500\text{ K}} - \frac{600\text{ kJ}}{200\text{ K}} = -1\text{ kJ/K}$ → $\boldsymbol{\sigma_{cycle} = +1\text{ kJ/K} > 0}$

Irreversibilities present within system

(b) $-\sigma_{cycle} = \frac{1000\text{ kJ}}{500\text{ K}} - \frac{600\text{ kJ}}{300\text{ K}} = 0\text{ kJ/K}$ → $\boldsymbol{\sigma_{cycle} = 0\text{ kJ/K} = 0}$

No irreversibilities present within system

(c) $-\sigma_{cycle} = \frac{1000\text{ kJ}}{500\text{ K}} - \frac{600\text{ kJ}}{400\text{ K}} = 0.5\text{ kJ/K}$ → $\boldsymbol{\sigma_{cycle} = -0.5\text{ kJ/K} < 0}$

Impossible