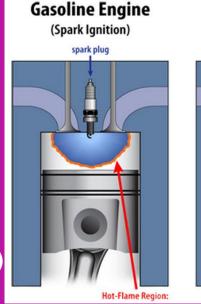
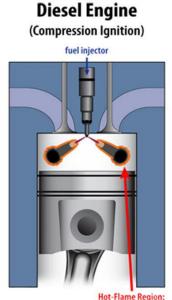
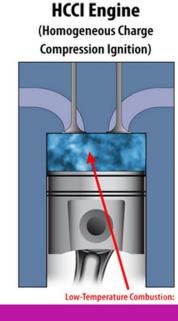
Thermodynamics

An Engineering Approach

Lecture 5: The Second Law of Thermodynamics









Qiang Cheng (Jonny)

Learning Outcomes

When you complete your study of this chapter, you will be able to...

explain 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.

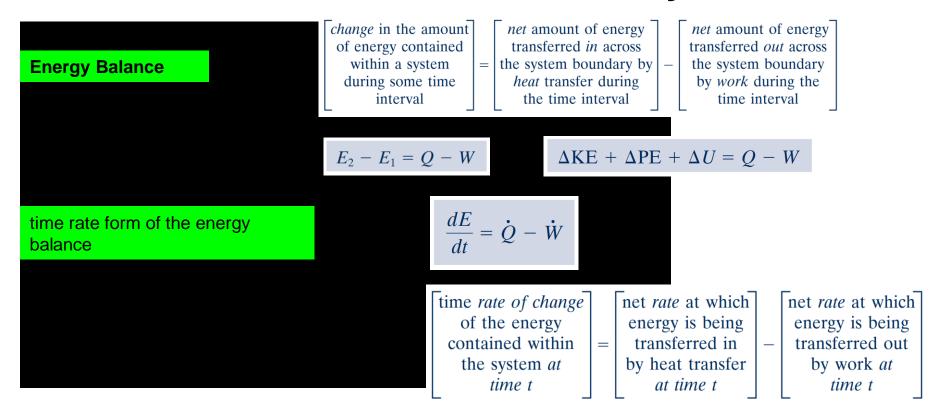
list several important irreversibilities.

evaluate the performance of power cycles and refrigeration and heat pump cycles

describe the Carnot cycle.



Recall the First Law of Thermodynamics





Introducing the Second Law

The foregoing discussion indicates that not every process consistent with the principle of energy conservation can occur.

Generally, an energy balance alone neither enables the preferred direction to be predicted nor permits the processes that can occur to be distinguished from those that cannot.

In elementary cases, such as the ones considered in Fig. 5.1, experience can be drawn upon to deduce whether particular spontaneous processes occur and to deduce their directions.

For more complex cases, where experience is lacking or uncertain, a guiding principle is necessary. This is provided by the second law.

The foregoing discussion also indicates that when left alone systems tend to undergo spontaneous changes until a condition of equilibrium is achieved, both internally and with their surroundings. In some cases equilibrium is reached quickly, whereas in others it is achieved slowly.



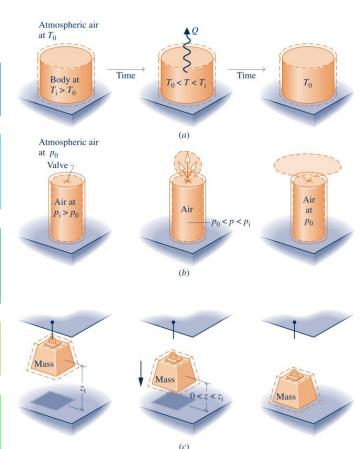
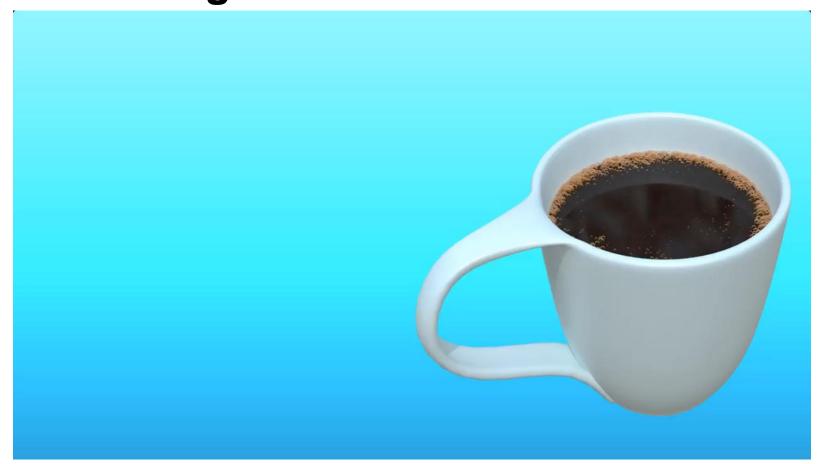


Fig. 5.1 Illustrations of spontaneous processes and the eventual attainment of equilibrium with the surroundings. (a) Spontaneous heat transfer. (b) Spontaneous expansion. (c) Falling mass.

Introducing the Second Law





Aspects of the Second Law

We conclude our introduction to the second law by observing that the second law and deductions from it have many important uses, including means for

Aspects of the Second Law

- 1. predicting the direction of processes.
- 2. establishing conditions for equilibrium.
- 3. determining the best theoretical performance of cycles, engines, and other devices.

TAKE NOTE...

No single statement of the second law brings out each of its many aspects.

- 4. evaluating quantitatively the factors that preclude the attainment of the best theoretical performance level.
- 5. defining a temperature scale independent of the properties of any thermometric substance.
- 6. developing means for evaluating properties such as u and h in terms of properties

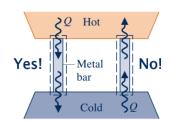


The six points listed can be thought of as aspects of the second law of thermodynamics and not as independent and unrelated ideas. Nonetheless, given the variety of these topic areas, it is easy to understand why there is no single statement of the second law that brings out each one clearly. There are several alternative, yet equivalent, formulations of the second law.

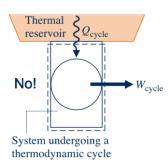
Statements of the Second Law

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.



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.

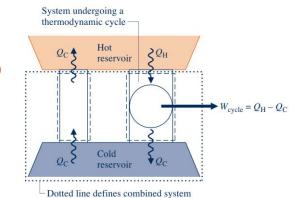


Entropy Statement of the Second Law

change in the amount of entropy contained within the system during some time interval net amount of entropy transferred in across the system boundary during the time interval

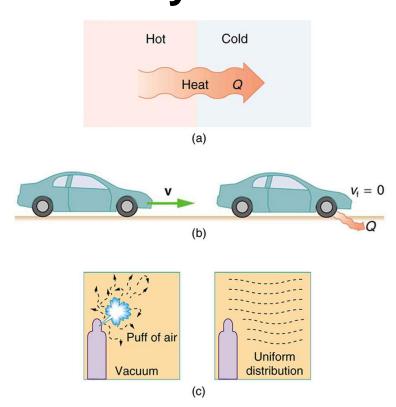
amount of entropy produced within the system during the time interval

(5.2)





Comparison of the First and Second Law of Thermodynamics



FIRST LAW OF THERMODYNAMICS VERSUS SECOND LAW OF THERMODYNAMICS

A version of the law States what types of conservation of of thermodynamic processes are energy forbidden in nature The entropy of an Energy can be isolated system neither created nor never decreases. destroyed $\Delta U = \Delta Q + \Delta W$ can be Calculate the used to calculate the maximum achievable algebraic value of one thermal efficiency of quantity if other two a given heat engine quantities are known Pediaa.com



Thermal Energy Reserviors

In the development of the second law of thermodynamics, it is very convenient to have a hypothetical body with a relatively large thermal energy capacity (mass x specific heat) that can supply or absorb finite amounts of heat without undergoing any change in temperature. Such a body is called a thermal energy reservoir.

A two-phase system can also be modeled as a reservoir since it can absorb and release large quantities of heat while remaining at constant temperature.

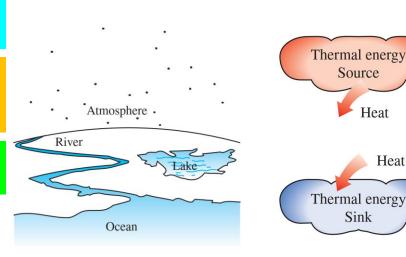
A body does not actually have to be very large to be considered a reservoir. Any physical body whose thermal energy capacity is large relative to the amount of energy it supplies or absorbs can be modeled as one.

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.

Thermal energy reservoirs are often referred to as heat reservoirs since they supply or absorb energy in the form of heat.

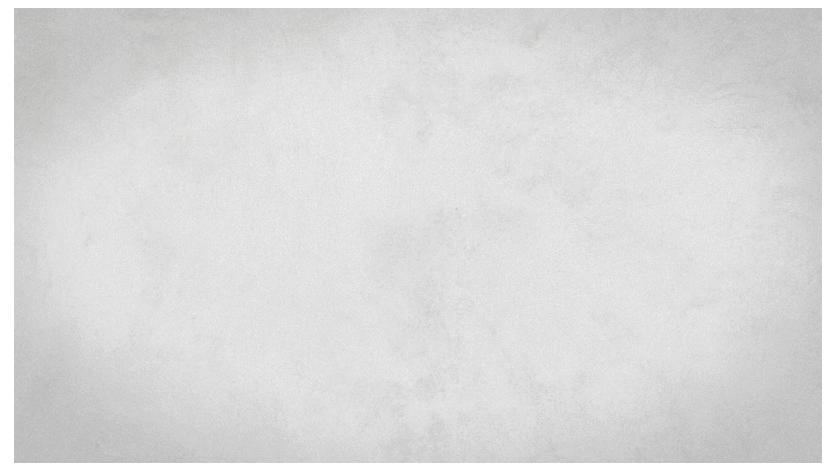
Heat transfer from industrial sources to the environment is of major concern to environmentalists as well as to engineers.





Heat

Irreversible and Reversible Processes





Irreversible and Reversible Processes

irreversible process

A process is called irreversible if the system and all parts of its surroundings cannot be exactly restored to their respective initial states after the process has occurred.

reversible process

A process is reversible if both the system and surroundings can be returned to their initial states.

irreversible processes normally include one or more of the following irreversibilities:

- 1. Heat transfer through a finite temperature difference
- 2. Unrestrained expansion of a gas or liquid to a lower pressure
- 3. Spontaneous chemical reaction
- 4. Spontaneous mixing of matter at different compositions or states
- 5. Friction—sliding friction as well as friction in the flow of fluids
- 6. Electric current flow through a resistance
- 7. Magnetization or polarization with hysteresis
- 8. Inelastic deformation



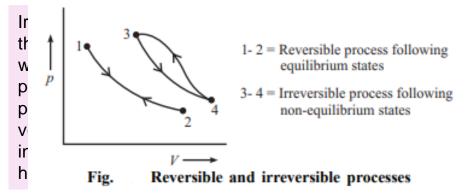
Although the foregoing list is not exhaustive, it does suggest that all actual processes are irreversible. That is, every process involves effects such as those listed, whether it is a naturally occurring process or one involving a device of our construction, from the simplest mechanism to the largest industrial plant.

Reversible and Irreversible Processes

Reversible Process

A <u>thermodynamic process</u> is reversible if the process can return back in such a that both the system and the surroundings return to their original states, with no other change anywhere else in the universe. It means both system and surroundings are returned to their initial states at the end of the reverse process.

Irreversible Process



REVERSIBLE PROCESS

VERSUS

IRREVERSIBLE PROCESS

A reversible process is a process that can be reversed in order to obtain the initial state of a system

An irreversible process is a thermodynamic process that cannot be reversed in order to obtain the initial state of a system

Can be reversed

Cannot be reversed

Infinite changes occur in the system

Finite changes occur in the system

There is an equilibrium between the initial state and the final state of the system There is no equilibrium in the system

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Second Law Aspects of Power Cycles Interacting with Two Reservoirs

Limit on Thermal Efficiency

$$\eta = \frac{W_{\text{cycle}}}{Q_{\text{H}}} = 1 - \frac{Q_{\text{C}}}{Q_{\text{H}}}$$

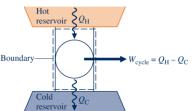


Fig. 5.5 System undergoing a power cycle while exchanging energy by heat transfer with two reservoirs.

In arriving at this conclusion, it was not necessary to

- identify the nature of the substance contained within the system,
- specify the exact series of processes making up the cycle,
- indicate whether the processes are actual processes or somehow idealized.

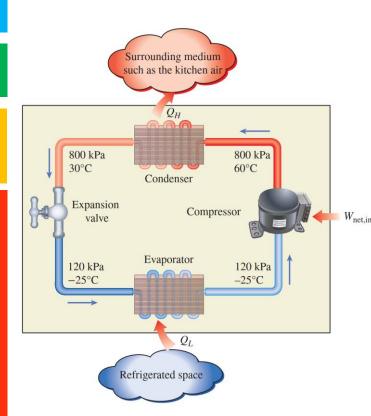


Regrigerators

The transfer of heat from a low-temperature medium to a high-temperature one requires special devices called refrigerators.

Refrigerators, like heat engines, are cyclic devices. The working fluid used in the refrigeration cycle is called a refrigerant.

The most frequently used refrigeration cycle is the vapor-compression refrigeration cycle, which involves four main components: a compressor, a condenser, an expansion valve, and an evaporator.



Regrigerators

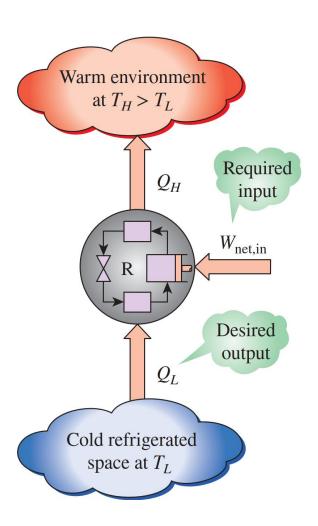
Coefficient of Performance

The efficiency of a refrigerator is expressed in terms of the coefficient of performance (COP), denoted by COP_R.

$$COP_{R} = \frac{Desired output}{Required input} = \frac{Q_{L}}{W_{net,in}} \qquad W_{net,in} = Q_{H} - Q_{L} \qquad (kJ)$$

$$COP_R = \frac{Q_L}{Q_H - Q_L} = \frac{1}{Q_H/Q_L - 1}$$

Notice that the value of COP_R can be greater than unity. That is, the amount of heat removed from the refrigerated space can be greater than the amount of work input. This is in contrast to the thermal efficiency, which can never be greater than 1.





EXAMPLE 5.2 ▶

Evaluating Refrigerator Performance

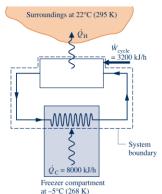
By steadily circulating a refrigerant at low temperature through passages in the walls of the freezer compartment, a refrigerator maintains the freezer compartment at -5° C when the air surrounding the refrigerator is at 22°C. The rate of heat transfer from the freezer compartment to the refrigerant is 8000 kJ/h and the power input required to operate the refrigerator is 3200 kJ/h. Determine the coefficient of performance of the refrigerator and compare with the coefficient of performance of a reversible refrigeration cycle operating between reservoirs at the same two temperatures.

SOLUTION

Known: A refrigerator maintains a freezer compartment at a specified temperature. The rate of heat transfer from the refrigerated space, the power input to operate the refrigerator, and the ambient temperature are known.

Find: Determine the coefficient of performance and compare with that of a reversible refrigerator operating between reservoirs at the same two temperatures.

Schematic and Given Data:



Engineering Model:

- 1. The system shown on the accompanying figure is at steady state.
- The freezer compartment and the surrounding air play the roles of cold and hot reservoirs, respectively.
- **3.** The energy transfers are positive in the directions of the arrows on the schematic.

Fig. E5.2

Analysis: Inserting the given operating data into Eq. 5.5 expressed on a *time-rate* basis, the coefficient of performance of the refrigerator is

$$\beta = \frac{\dot{Q}_{\rm C}}{\dot{W}_{\rm cycle}} = \frac{8000 \text{ kJ/h}}{3200 \text{ kJ/h}} = 2.5$$



Substituting values into Eq. 5.10 gives the coefficient of performance of a reversible refrigeration cycle operating between reservoirs at $T_{\rm C}=268~{\rm K}$ and $T_{\rm H}=295~{\rm K}$ as

- $\beta_{\text{max}} = \frac{T_{\text{C}}}{T_{\text{H}} T_{\text{C}}} = \frac{268 \text{ K}}{295 \text{ K} 268 \text{ K}} = 9.9$
- ② In accord with the corollaries of Sec. 5.7.2, the coefficient of performance of the refrigerator is less than for a reversible refrigeration cycle operating between reservoirs at the same two temperatures. That is, irreversibilities are present within the system.
- 1 The temperatures T_C and T_H used in evaluating β_{max} must be in K or ${}^{\circ}R$.
- 2 The difference between the actual and maximum coefficients of performance suggests that there may be some potential for improving the thermodynamic performance. This objective should be approached judiciously, however, for improved performance may require increases in size, complexity, and cost.

Quick Quiz

An inventor claims the power required to operate the refrigerator can be reduced to 800 kJ/h while all other data remain the same.

Evaluate this claim using the second law. Ans. $\beta = 10$. Claim invalid.



□ apply the second law corollaries of Sec. 5.7.2, using Eqs. 5.5 and 5.10 appropriately.

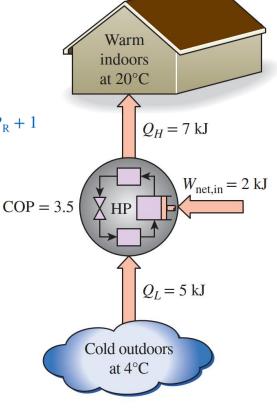
Heat Pumps

Another device that transfers heat from a low-temperature medium to a hightemperature one is the heat pump. Refrigerators and heat pumps operate on the same cycle but differ in their objectives.

$$COP_{HP} = \frac{Desired output}{Required input} = \frac{Q_H}{W_{net,in}}$$

$$COP_{HP} = \frac{Q_H}{Q_H - Q_L} = \frac{1}{1 - Q_L/Q_H}$$
 $COP_{HP} = COP_R + 1$





EXAMPLE 5.3 ▶

Evaluating Heat Pump Performance

A building requires 5×10^5 Btu per day to maintain its temperature at 70° F when the outside temperature is 32° F. (a) If an electric heat pump is used to supply this energy, determine the minimum theoretical work input for one day of operation, in Btu/day. (b) Evaluating electricity at 13 cents per kW·h, determine the minimum theoretical cost to operate the heat pump, in \$/day.

SOLUTION

Known: A heat pump maintains a building at a specified temperature. The energy supplied to the building, the ambient temperature, and the unit cost of electricity are known.

Find: Determine the minimum theoretical work required by the heat pump and the corresponding electricity cost.

Schematic and Given Data:

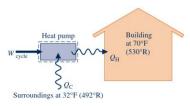


Fig. E5.3

Engineering Model:

- **1.** The system shown on the accompanying figure executes a heat pump cycle.
- The building and the outside air play the roles of hot and cold reservoirs, respectively.
- 3. The value of electricity is 13 cents per kW · h.
- The energy transfers are positive in the directions of the arrows on the schematic.

Analysis:

(a) Using Eq. 5.6, the work for any heat pump cycle can be expressed as $W_{\rm cycle} = Q_{\rm H}/\gamma$. The coefficient of performance γ of an actual heat pump is less than, or equal to, the coefficient of performance $\gamma_{\rm max}$ of a reversible heat pump cycle when each operates between the same two thermal reservoirs: $\gamma \leq \gamma_{\rm max}$. Accordingly, for a given value of $Q_{\rm H}$

$$W_{\text{cycle}} \ge \frac{Q_{\text{H}}}{\gamma_{\text{max}}}$$

With Eq. 5.11

0

$$\gamma_{\text{max}} = \frac{T_{\text{H}}}{T_{\text{H}} - T_{\text{C}}} = \frac{530^{\circ} \text{R}}{38^{\circ} \text{R}} = 13.95$$

Collecting results

$$W_{\text{cycle}} \ge \frac{5 \times 10^5 \text{ Btu/day}}{13.95} = 3.58 \times 10^4 \frac{\text{Btu}}{\text{day}}$$

The *minimum* theoretical work input is 3.58×10^4 Btu/day.

(b) Using the result of part (a) together with the given cost data and an appropriate conversion factor,

$$\begin{bmatrix} \text{minimum} \\ \text{theoretical} \\ \text{cost per day} \end{bmatrix} = \left(3.58 \times 10^4 \frac{\text{Btu}}{\text{day}} \left| \frac{1 \text{ kW} \cdot \text{h}}{3413 \text{ Btu}} \right| \right) \left(0.13 \frac{\$}{\text{kW} \cdot \text{h}}\right) = 1.36 \frac{\$}{\text{day}}$$



Ability to...

□ apply the second law corollaries of Sec. 5.7.2, using Eqs. 5.6 and 5.11 appropriately.

conduct an elementary economic evaluation.

- 1 Note that the temperatures T_C and T_H must be in ${}^{\circ}R$ or K.
- 2 Because of irreversibilities, an actual heat pump must be supplied more work than the minimum to provide the same heating effect. The actual daily cost could be substantially greater than the minimum theoretical cost.



Heat Engine

Work can be converted to heat directly and completely, but converting heat to work requires the use of some special devices. These devices are called heat engines.

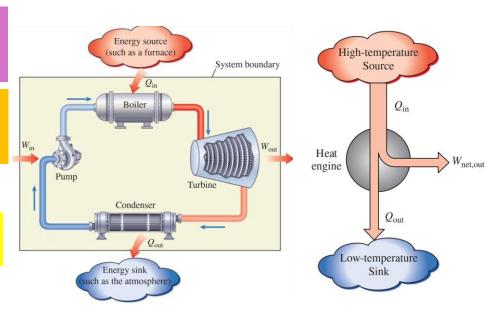
The net work output of this power plant is simply the difference between the total work output of the plant and the total work input

$$W_{\text{net,out}} = W_{\text{out}} - W_{\text{in}}$$
 (kJ)

Heat engines differ considerably from one another, but all can be characterized by the following:

- 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.





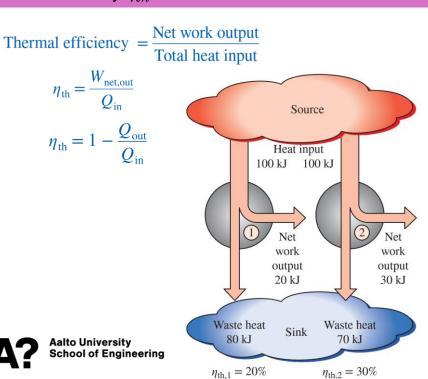
Recall that for a closed system undergoing a cycle, the change in internal energy ΔU is zero, and therefore the net work output of the system is also equal to the net heat transfer to the system:

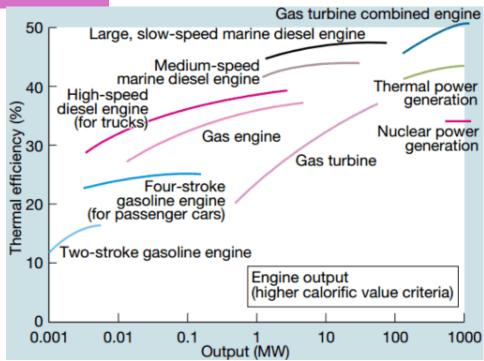
$$W_{\text{net.out}} = Q_{\text{in}} - Q_{\text{out}}$$
 (kJ)

Heat Engine

Thermal Efficiency

The fraction of the heat input that is converted to net work output is a measure of the performance of a heat engine and is called the thermal efficiency η_{th}





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Evaluating Power Cycle Performance

A power cycle operating between two thermal reservoirs receives energy $Q_{\rm H}$ by heat transfer from a hot reservoir at $T_{\rm H}=2000~{\rm K}$ and rejects energy $Q_{\rm C}$ by heat transfer to a cold reservoir at $T_{\rm C}=400~{\rm K}$. For each of the following cases determine whether the cycle operates reversibly, operates irreversibly, or is impossible.

(a)
$$Q_{\rm H} = 1000 \text{ kJ}, \eta = 60\%$$

(b)
$$Q_{\rm H} = 1000 \text{ kJ}, W_{\rm cycle} = 850 \text{ kJ}$$

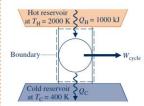
(c)
$$Q_{\rm H} = 1000 \text{ kJ}, Q_{\rm C} = 200 \text{ kJ}$$

SOLUTION

Known: A system operates in a power cycle while receiving energy by heat transfer from a reservoir at 2000 k and discharging energy by heat transfer to a reservoir at 400 K.

Find: For each of three cases determine whether the cycle operates reversibly, operates irreversibly, or is impossible

Schematic and Given Data:



Engineering Model:

- 1. The system shown in the accompanying figure executes a power cycle.
- 2. Each energy transfer is positive in the direction of the arrow.

Fig. E5.1



Analysis: The maximum thermal efficiency for *any* power cycle operating between the two thermal reservoirs is given by Eq. 5.9. With the specified temperatures

- $\eta_{\text{max}} = 1 \frac{T_{\text{C}}}{T_{\text{H}}} = 1 \frac{400 \text{ K}}{2000 \text{ K}}$ = 0.8 (80%)
- (a) The given thermal efficiency is $\eta = 60\%$. Since $\eta < \eta_{max}$, the cycle operates irreversibly.
- (b) Using given the data, $Q_{\rm H}=1000~{\rm kJ}$ and $W_{\rm cycle}=850~{\rm kJ}$, the thermal efficiency is

$$\eta = \frac{W_{\text{cycle}}}{Q_{\text{H}}} = \frac{850 \text{ kJ}}{1000 \text{ kJ}} \\
= 0.85 (85\%)$$

Since $\eta > \eta_{\text{max}}$, the power cycle is impossible.

(c) Applying an energy balance together with the given data,

$$W_{\text{cycle}} = Q_{\text{H}} - Q_{\text{C}}$$

= 1000 kJ - 200 kJ = 800 kJ

The thermal efficiency is then

0

$$\eta = \frac{W_{\text{cycle}}}{Q_{\text{H}}} = \frac{800 \text{ kJ}}{1000 \text{ kJ}}$$

$$= 0.80 (80\%)$$

Since $\eta = \eta_{\text{max}}$, the cycle operates reversibly.



apply the Carnot corollaries, using Eqs. 5.4 and 5.9 appropriately

1) The temperatures $T_{\rm C}$ and $T_{\rm H}$ used in evaluating $\eta_{\rm max}$ must be in K or ${}^{\circ}{\rm R}$.

uick Quiz If $Q_{\rm C}=300$ kJ and $W_{\rm cycle}=2700$ kJ, determine whether the power cycle operates reversibly, operates irreversibly, or is impossible. Ans. Impossible.

Carnot cycle

Carnot cycle

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.

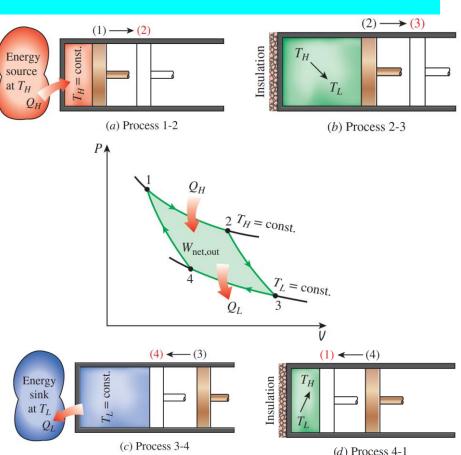
Process 1–2: The gas is compressed adiabatically to state 2, where the temperature is TH.

Process 2–3: The assembly is placed in contact with the reservoir at TH. The gas expands isothermally while receiving energy QH from the hot reservoir by heat transfer.

Process 3–4: The assembly is again placed on the insulating stand and the gas is allowed to continue to expand adiabatically until the temperature drops to TC.

Process 4–1: The assembly is placed in contact with the reservoir at TC. The gas is compressed isothermally to its initial state while it discharges energy QC to the cold reservoir by heat transfer.



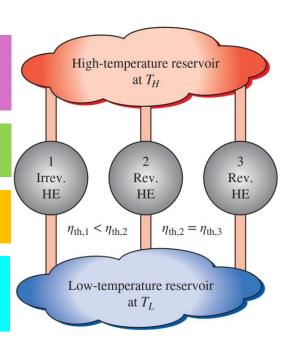


The Carnot Principles

Two conclusions pertain to the thermal efficiency of reversible and irreversible (i.e., actual) heat engines, and they are known as the Carnot principles, expressed as follows:

- 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.

we conclude that no reversible heat engine can be more efficient than a reversible one operating between the same two reservoirs, regardless of how the cycle is completed or the kind of working fluid used.





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.

The second Carnot principle states that all reversible heat engines have the same thermal efficiency when operating between the same two reservoirs

Since energy reservoirs are characterized by their temperatures, the thermal efficiency of reversible heat engines is a function of the reservoir temperatures only.

$$\eta_{\text{th,rev}} = g(T_H, T_L)$$

$$\frac{Q_H}{Q_L} = f(T_H, T_L)$$

For three engines separately, we obtain

$$\frac{Q_1}{Q_2} = f(T_1, T_2), \quad \frac{Q_2}{Q_3} = f(T_2, T_3), \quad \text{and} \quad \frac{Q_1}{Q_3} = f(T_1, T_3) \quad \frac{Q_1}{Q_3} = \frac{Q_1}{Q_2} \frac{Q_2}{Q_3}$$

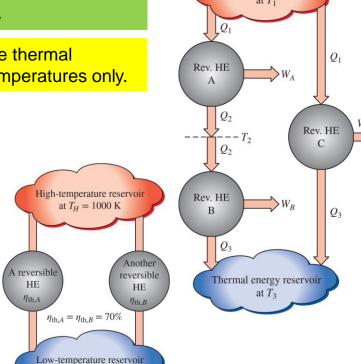
$$f(T_1, T_3) = f(T_1, T_2) \cdot f(T_2, T_3)$$

• This condition will be satisfied only if the function *f* has the following form:

$$f(T_1, T_2) = \frac{\phi(T_1)}{\phi(T_2)}$$
 and $f(T_2, T_3) = \frac{\phi(T_2)}{\phi(T_3)}$



$$\frac{Q_1}{Q_2} = f(T_1, T_3) = \frac{\phi(T_1)}{\phi(T_3)}$$



at $T_L = 300 \text{ K}$

Thermal energy reservoir

The Thermodynamic Temperature Scale

 For a reversible heat engine operating between two reservoirs at temperatures TH and TL,

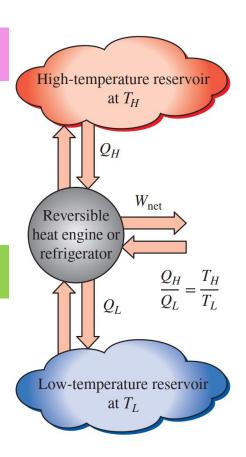
$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)}$$

Temperature Scale (or Kelvin Scale)

$$\left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$$

• For a reversible heat engine operating between two reservoirs at temperatures TH and TL, can be written as

$$\frac{Q_H}{Q_L} = \frac{\phi(T_H)}{\phi(T_L)} \qquad \left(\frac{Q_H}{Q_L}\right)_{\text{rev}} = \frac{T_H}{T_L}$$





The Carnot Heat Engine

The thermal efficiency of any heat engine, reversible or irreversible, is given by

$$\eta_{\rm th} = 1 - \frac{Q_L}{Q_H}$$

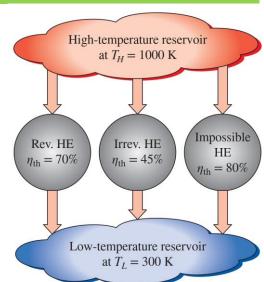
For reversible heat engines, the heat transfer ratio in the preceding relation can be replaced by the ratio of the absolute temperatures of the two reservoirs

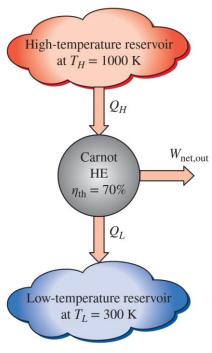
$$\eta_{\rm th,rev} = 1 - \frac{T_L}{T_H}$$

The thermal efficiencies of actual and reversible heat engines operating between the same temperature limits compare as follows

$$\eta_{\text{th}} \begin{cases}
< \eta_{\text{th,rev}} \\
= \eta_{\text{th,rev}} \\
> \eta_{\text{th,rev}}
\end{cases}$$

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







The Carnot Refrigerator and Heat Pump

• The coefficient of performance of any refrigerator or heat pump, reversible or irreversible, is given by

$$COP_R = \frac{1}{Q_H/Q_L - 1} \quad \text{and} \quad COP_{HP} = \frac{1}{1 - Q_L/Q_H}$$

• The COPs of all reversible refrigerators or heat pumps can be determined by replacing the heat transfer ratios in the preceding relations with the ratios of the absolute temperatures of the high- and low-temperature reservoirs. Then the COP relations for reversible refrigerators and heat pumps become

$$COP_{R,rev} = \frac{1}{T_H/T_L - 1} \qquad COP_{HP,rev} = \frac{1}{1 - T_L/T_H}$$

 The coefficients of performance of actual and reversible refrigerators operating between the same temperature limits can be compared as follows:

$$COP_{R} \begin{cases} < & COP_{R,rev} & irreversible refrigerator \\ = & COP_{R,rev} & reversible refrigerator \\ > & COP_{R,rev} & impossible refrigerator \end{cases}$$



