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Chapter 20

The Second Law of Thermodynamics

University Physics with
Modern Physics
Third Edition

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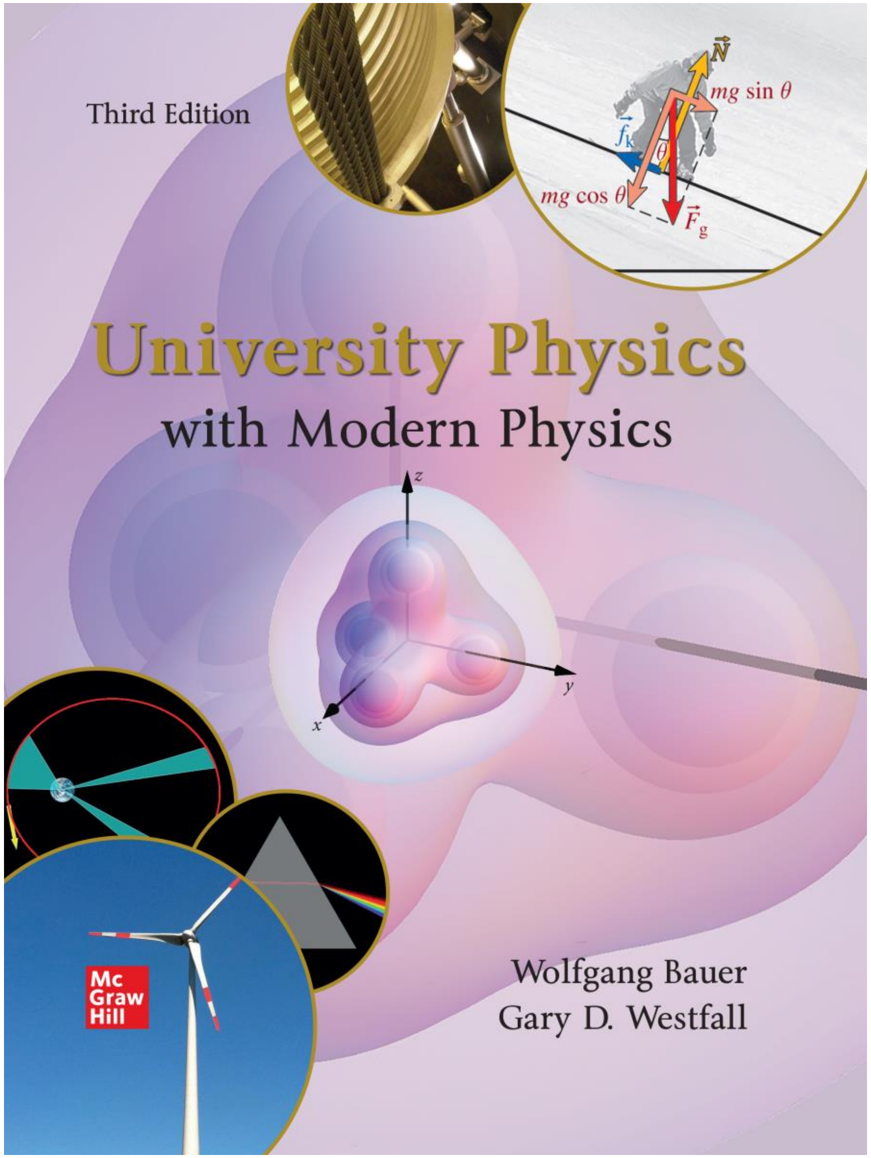

The Second Law of Thermodynamics

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The Second Law of Thermodynamics

- In this chapter, we examine heat engines in theory and in practice.

- Their operation is governed by the Second Law of Thermodynamics—one of the most far-reaching and powerful statements in all of science.

- There are several different ways to express this law, including one involving a concept called *entropy*.

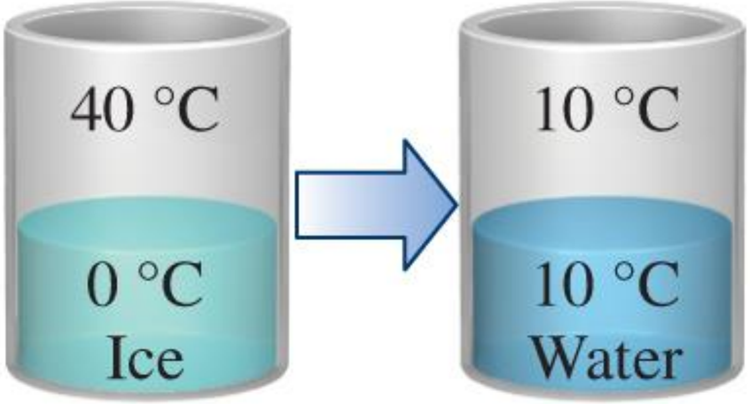
- The ideas discussed in this chapter have applications to practically all areas of science, including information processing, biology, and astronomy.

Reversible and Irreversible Processes 1

- If you pour hot water into a glass and place that glass on a table, the water will slowly cool until it reaches the temperature of its surroundings.
- The air in the room will also warm.
- You would be astonished if, instead, the water got warmer and the air in the room cooled down slightly, while conserving energy.
- The First Law of Thermodynamics is satisfied for both scenarios.
- It is always the case that the water cools until it reaches the temperature of its surroundings.
- Other physical principles are required to explain why the temperature changes one way and not the other.

Reversible and Irreversible Processes 2

- Practically all real-life thermodynamic processes are irreversible.
- For example, if a disk of ice at a temperature of 0 °C is placed in a metal can having a temperature of 40 °C, heat flows irreversibly from the can to the ice.
- The ice will melt to water; the water will then warm, and the can will cool, until the water and the can are at the same temperature.
- It is not possible to make small changes in any thermodynamic variable and return the system to the state corresponding to a warm can and frozen water.



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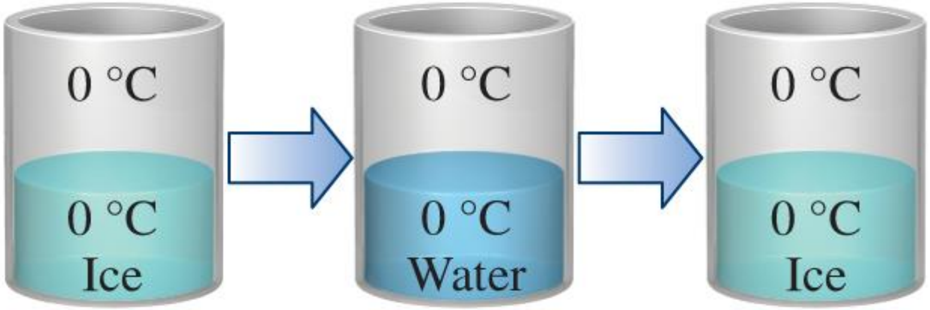
Reversible and Irreversible Processes 3

- We can imagine a class of idealized reversible processes.
- With a reversible process, a system is always close to being in thermodynamic equilibrium.
- Making a small change in the state of the system can reverse any change in the thermodynamic variables of the system.
- For example, a disk of ice at a temperature of 0 °C is placed in a metal can that is also at a temperature of 0 °C.
- Raising the temperature of the can slightly will melt the ice to water.
- Then, lowering the temperature of the metal can will refreeze the water to ice, thus returning the system to its original state.



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Reversible and Irreversible Processes 4

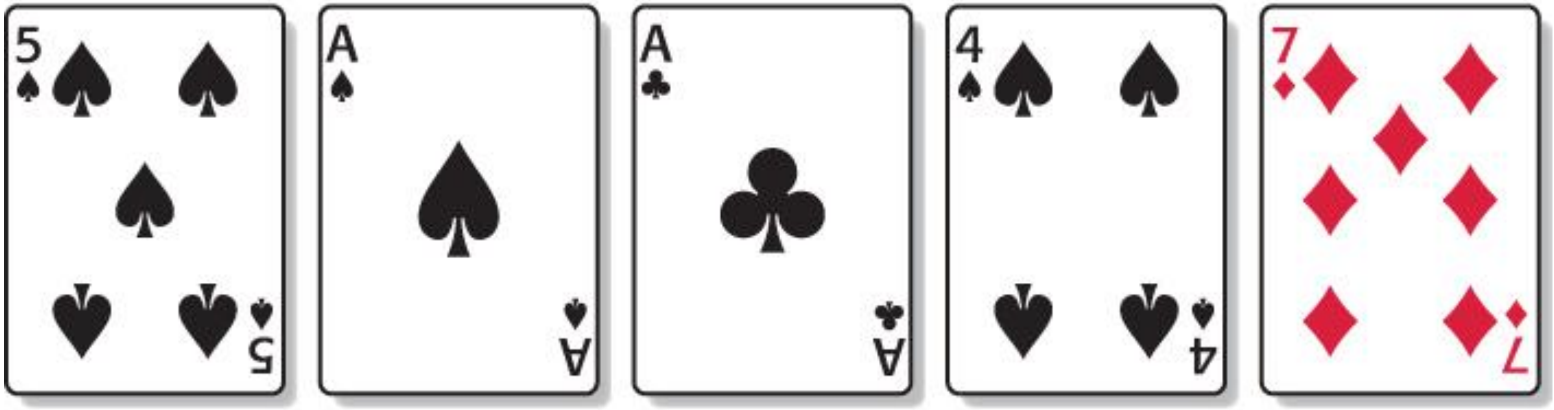
- We can think of reversible processes as equilibrium processes in which the system always stays in, or close to, thermal equilibrium.
- If a system were in thermal equilibrium, no heat would flow, and no work would be done by the system.
- Thus, a reversible process is an idealization. However, for a nearly reversible process, small temperature and pressure adjustments can keep a system close to thermal equilibrium.
- On the other hand, if a process involves heat flow with a finite temperature difference free expansion of a gas, or conversion of mechanical work to thermal energy, it is an **irreversible process**.

Reversible and Irreversible Processes 5

- It is not possible to make small changes to the temperature or pressure of the system and cause the process to proceed in the opposite direction.
- In addition, while an irreversible process is taking place, the system is not in thermal equilibrium.
- The irreversibility of a process is related to the randomness or disorder of the system.
- For example, suppose you order a deck of cards by rank and suit and then take the first five cards:

Reversible and Irreversible Processes 6

- Next, you put those five cards back in the deck, toss the deck of cards in the air, and let the cards fall on the floor.
- You pick up the cards one by one without looking at their rank or suit and then take the first five cards off the top of the deck.
- It is highly improbable that these five cards will be ordered by rank and suit.
- It is much more likely that you will see a result like:



Poincaré Recurrence Time

- Have you ever experienced déjà vu?
- If processes leading from one event to another are truly irreversible, then an event cannot repeat exactly.
- The French mathematician and physicist Henry Poincaré made an important contribution to this discussion in 1890, by famously stating his recurrence theorem.
- In it he postulates that certain isolated dynamical systems will return to a state arbitrarily close to their initial state after a sufficiently long time.
- This time is known as the *Poincaré recurrence time*, or simply the *Poincaré time*, of the system.
- This time can be calculated straightforwardly for many systems that have only a finite number of different states, as the following example illustrates.

Deck of Cards 1

- Suppose you repeat the tossing and gathering of a deck of cards again and again.
- Eventually, there is a chance that one of the random orders in which you pick up the cards will yield the sequence ace through ten of spades for the first five cards in the deck.

PROBLEM:

- If it takes 1 min on average to toss the cards into the air and then collect them into a stack again, how long can you expect it to take, on average, before you will find the sequence of ace through ten of spades as the first five cards in the deck?

SOLUTION:

- There are 52 cards in the deck.

Deck of Cards 2

- Each of them has the same 1/52 probability of being on top.
- So, the probability that the ace of spades ends up on top is 1/52.
- If the ace is the top card, then there are 51 cards left.
- The probability that the king of spades is in the top position of the remaining 51 cards is 1/51.
- The combined probability that the ace and king of spades are the top two cards in that order is $1/(52 \cdot 51) = 1/2652$.
- In the same way, the probability of the ordered sequence of ace through ten of spades occurring is $1/(52 \cdot 51 \cdot 50 \cdot 49 \cdot 48) =$ 1/311,875,200.
- So, the average number of tries needed to obtain the desired sequence is 311,875,200.

Deck of Cards 3

- Since each of them takes 1 min, successful completion of this exercise would take approximately 593 yr (24/7).

  DISCUSSION:

- We can almost immediately state the average number of tries it would take to get all 52 cards in the ordered sequence ace through two, for all four suits.
- It is 52·51·50· … ·3·2·1 = 52!
- If each of these attempts took a minute, it would require an average of $1.534 \cdot 10^{62}$ yr to obtain the desired order.
- But even after this time, there would be no guarantee that the ordered sequence had to appear.
- However, since there are 52! possible different sequences of the cards in the deck, at least one of the sequences would have appeared at least twice.

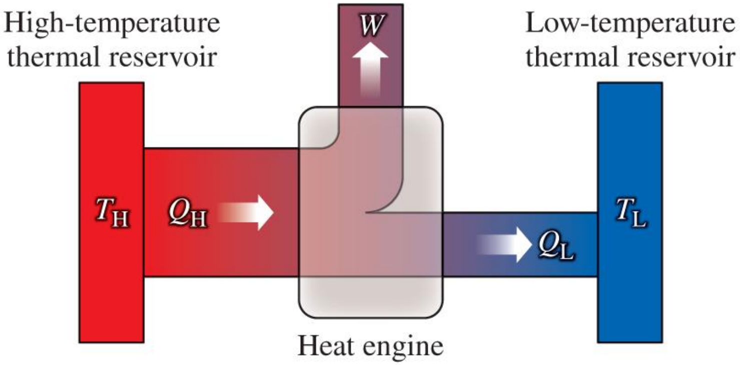
Engines and Refrigerators 1

- A **heat engine** is a device that turns thermal energy into useful work.
- For example, an internal combustion engine or a jet engine extracts mechanical work from the thermal energy generated by burning a gasoline-air mixture.
- For a heat engine to do work repeatedly, it must operate in a cycle.
- For example, work would be done if you put a firecracker under a soup can and exploded the firecracker.
- The thermal energy from the explosion would be turned into mechanical motion of the soup can.
- However, the applications of this firecracker/soup-can engine are limited.

Engines and Refrigerators 2

- An engine that operates in a cycle passes through various thermodynamic states and returns to its original state.
- The cyclic processes that heat engines utilize always involve some kind of temperature change.
- We can think of the most basic heat engine as operating between two thermal reservoirs:

(a)



(b)

a: Monty Rakusen/Getty Images

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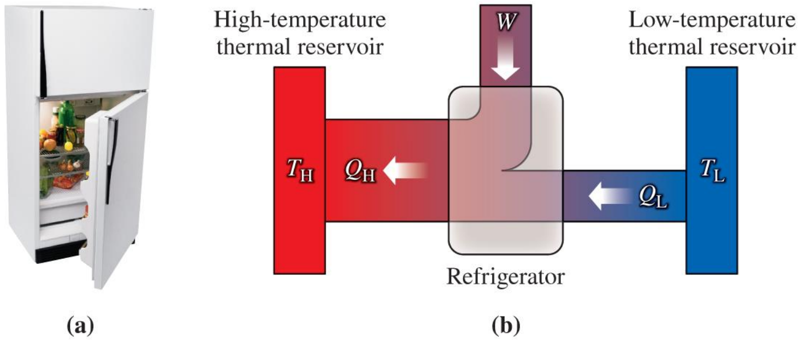
Engines and Refrigerators 3

- The engine takes heat, Q_{H}, from the high-temperature reservoir, turns some of that heat into mechanical work, W, and exhausts the remaining heat, Q_{L} (where $Q_{\mathrm{L}} > 0$), to the low-temperature reservoir.
- According to the First Law of Thermodynamics (equivalent to the conservation of energy), $Q_{\mathrm{H}} = W + Q_{\mathrm{L}}$.
- Thus, to make an engine operate, it must be supplied energy in the form of Q_{H}, and then it will return useful work, W.
- The efficiency, ε, of an engine is defined as:

$$\varepsilon = \frac{W}{Q_{\mathrm{H}}}$$

Engines and Refrigerators 4

- A refrigerator is a heat engine that operates in reverse.



a: C Squared Studios/Photodisc/Getty Images

- The refrigerator uses work to move heat from a low-temperature to a high-temperature thermal reservoir.
- In a real refrigerator, an electric motor drives a compressor, which transfers thermal energy from the interior of the refrigerator to the air in the room.

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Concept Check 1

- A refrigerator operates by

A. doing work to move heat from a low-temperature thermal reservoir to a high-temperature thermal reservoir.

B. doing work to move heat from a high-temperature thermal reservoir to a low-temperature thermal reservoir.

C. using thermal energy to produce useful work.

D. moving heat from a low-temperature thermal reservoir to a high-temperature thermal reservoir without doing work.

E. moving heat from a high-temperature thermal reservoir to a low-temperature thermal reservoir without doing work.

Solution Concept Check 1

- A refrigerator operates by

A. doing work to move heat from a low-temperature thermal reservoir to a high-temperature thermal reservoir.

B. doing work to move heat from a high-temperature thermal reservoir to a low-temperature thermal reservoir.

C. using thermal energy to produce useful work.

D. moving heat from a low-temperature thermal reservoir to a high-temperature thermal reservoir without doing work.

E. moving heat from a high-temperature thermal reservoir to a low-temperature thermal reservoir without doing work.

Engines and Refrigerators 5

- For a refrigerator, the First Law of Thermodynamics requires that $Q_\text{L} + W = Q_\text{H}$.
- It is desired that a refrigerator remove as much heat as possible from the cooler reservoir, Q_L , given the work, W, put into the refrigerator.
- The coefficient of performance, K, of a refrigerator is:

$$K = \frac{Q_\text{L}}{W}$$

- In the United States, refrigerators are usually rated by their annual energy usage, without quoting their actual efficiency.
- An efficient refrigerator is one whose energy use is comparable to the lowest energy use in its capacity class.

Engines and Refrigerators 6

- Air conditioners are often rated in terms of an energy efficiency rating (EER), defined as the heat removal capacity, *H*, in BTU/hour divided by the power *P* used in watts.
- The relationship between *K* and EER is:

$$K = \left|\frac{Q_\mathrm{L}}{W}\right| = \frac{Ht}{Pt} = \frac{H}{P} = \frac{\mathrm{EER}}{3.41}$$

- The factor 1/3.41 arises from the definition of a BTU per hour:

$$\frac{1\ \mathrm{BTU/h}}{1\ \mathrm{watt}} = \frac{(1055\ \mathrm{J})/(3600\ \mathrm{s})}{1\ \mathrm{J/s}} = \frac{1}{3.41}$$

Engines and Refrigerators 7

- Typical EER values for a room air conditioner range from 8 to 11, meaning that values of *K* range from 2.3 to 3.2.
- Thus, a typical room air conditioner can remove about three units of heat for every unit of energy used.
- Central air conditioners are often rated by a seasonally adjusted energy efficiency rating (SEER) that considers how long the air conditioner operates during a year.
- A **heat pump** is a variation of a refrigerator that can be used to warm buildings.
- The heat pump warms the building by cooling the outside air.
- Just as for a refrigerator, $Q_\mathrm{L} + W = Q_\mathrm{H}$.

Engines and Refrigerators 8

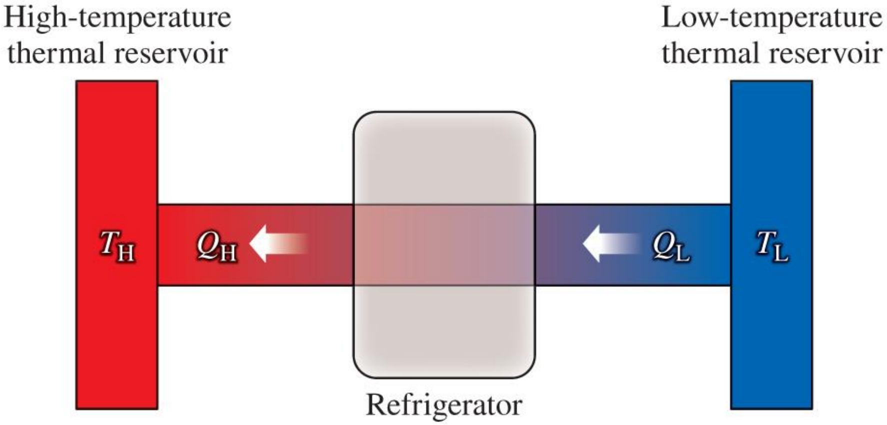
- For a heat pump, the quantity of interest is the heat put into the warmer reservoir, Q_{H}, rather than the heat removed from the cooler reservoir.
- Thus, the coefficient of performance of a heat pump is:

$$K_{\text{heat pump}} = \frac{Q_{\mathrm{H}}}{W}$$

- The typical coefficient of performance of a commercial heat pump ranges from 3 to 4.
- Heat pumps do not work well when the outside temperature goes below −18 °C (0 °F).

Concept Check 2

- Can a heat engine like the one shown in the figure operate?



A. yes
B. no
C. need to know the specific cycle used by the engine to answer
D. yes, but only with a monatomic gas
E. yes, but only with a diatomic gas

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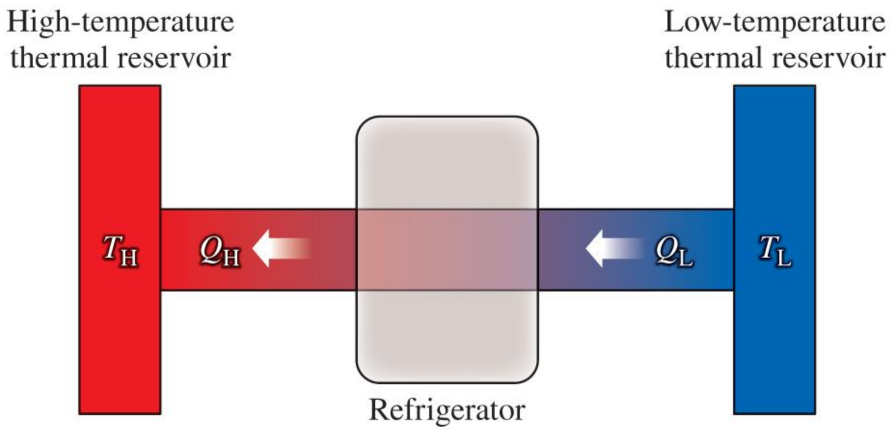
Solution Concept Check 2

- Can a heat engine like the one shown in the figure operate?



A. yes
B. [✓ no]
C. need to know the specific cycle used by the engine to answer
D. yes, but only with a monatomic gas
E. yes, but only with a diatomic gas

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Warming a House with a Heat Pump 1

- A heat pump with a coefficient of performance of 3.500 is used to warm a house that loses 75,000. BTU/h of heat on a cold day.
- Assume that the cost of electricity is 10.00 cents per kilowatt-hour.

PROBLEM:

- How much does it cost to warm the house for the day?

SOLUTION:

- The coefficient of performance of a heat pump is:

$$K_{\text{heat pump}} = \frac{Q_{\text{H}}}{W}$$

Warming a House with a Heat Pump 2

- The work required to warm the house is then:

$$W = \frac{Q_{\mathrm{H}}}{K_{\text{heat pump}}}$$

- The house is losing 75,000 BTU/h, which converts to:

$$\frac{75{,}000\ \mathrm{BTU}}{1\ \mathrm{h}} = \frac{1055\ \mathrm{J}}{1\ \mathrm{BTU}}\frac{1\ \mathrm{h}}{3600\ \mathrm{s}} = 21.98\ \mathrm{kW}$$

- The power required to warm the house is:

$$P = \frac{W}{t} = \frac{Q_{\mathrm{H}}/t}{K_{\text{heat pump}}} = \frac{21.98\ \mathrm{kW}}{3.500} = 6.280\ \mathrm{kW}$$

- The cost to warm the house is:

$$\mathrm{Cost} = (6.280\ \mathrm{kW})(24\ )\frac{\$0.1000}{1\ \mathrm{kWh}} = \$15.07$$

Ideal Engines

- An ideal engine is one that utilizes only reversible processes.
- Thus, the engine incorporates no “energy-wasting” effects, such as friction or viscosity.
- A heat engine is a device that turns thermal energy into useful work.
- You might think that an ideal engine would be 100% efficient.
- However, we’ll see that even the most efficient ideal engine cannot accomplish this.
- This fundamental inability to convert thermal energy totally into useful mechanical work lies at the very heart of the Second Law of Thermodynamics and of entropy, the two main topics of this chapter.

Concept Check 3

- An ideal heat engine is one that
  A. uses only reversible processes.
  B. uses only irreversible processes.
  C. has an efficiency of 100%.
  D. has an efficiency of 50%.
  E. does no work.

Solution Concept Check 3

- An ideal heat engine is one that

A. uses only reversible processes.

B. uses only irreversible processes.

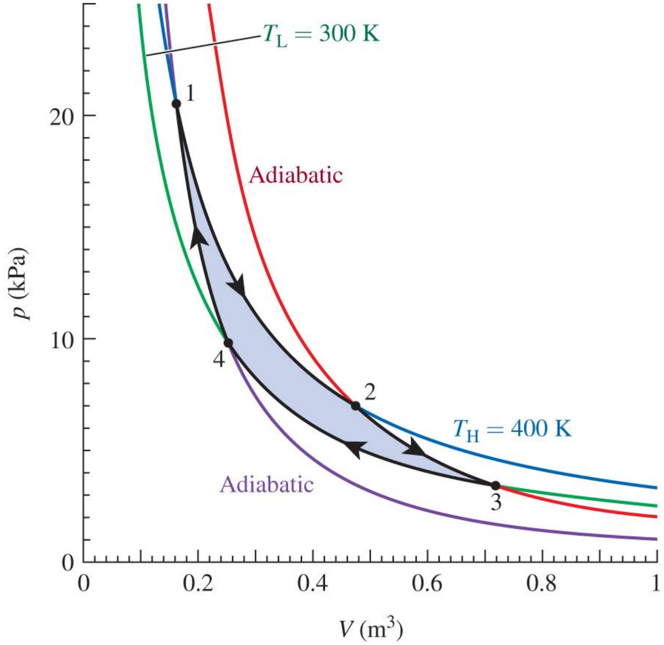
C. has an efficiency of 100%.

D. has an efficiency of 50%.

E. does no work.

Carnot Cycle 1

- An example of an ideal engine is the **Carnot engine**, which is the most efficient engine that operates between two temperature reservoirs and the only one to do so reversibly.
- The cycle of thermodynamic processes used by the Carnot engine is called the **Carnot cycle**.
- To be reversible, a Carnot cycle consists of two isothermal processes and two adiabatic processes.
- We can pick an arbitrary starting point for the cycle.
- Let's say that it begins at point 1.



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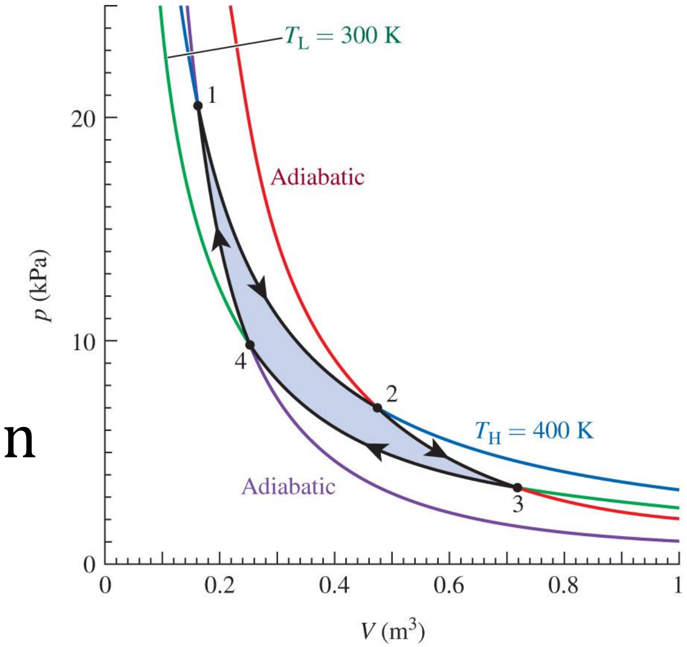
Carnot Cycle 2

- The system first undergoes an isothermal process, during which the system expands and absorbs heat from a thermal reservoir at fixed temperature T_H.
- At point 2, the system begins an adiabatic expansion.
- At point 3, the system begins another isothermal process, this time giving up heat to a second thermal reservoir at a lower temperature, T_L.
- At point 4, the system begins a second adiabatic process.
- The Carnot cycle is complete when the system returns to point 1.



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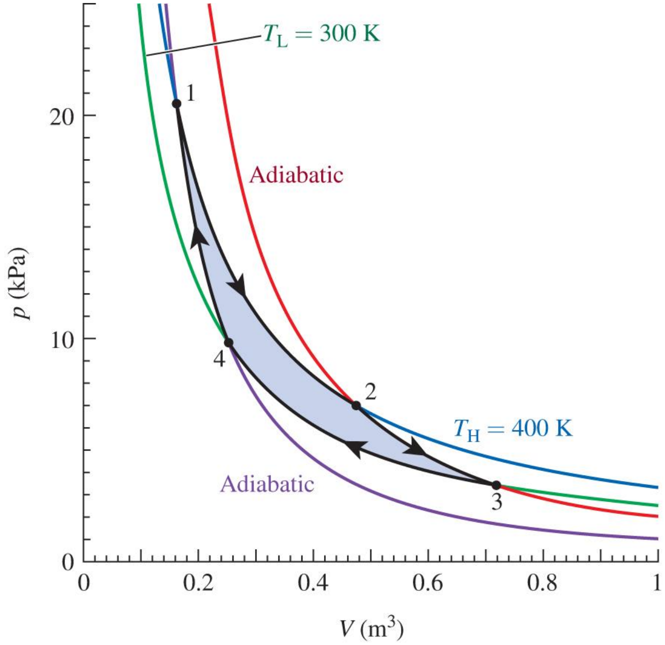
Carnot Cycle 3

- The efficiency of the Carnot engine is not 100% but instead is given by:

$$\varepsilon = 1 - \frac{T_\text{L}}{T_\text{H}}$$

- Remarkably, the efficiency of a Carnot engine depends only on the temperature ratio of the two thermal reservoirs (Deriv. 20.1).
- For the engine shown, the efficiency is $\varepsilon = 1 - (300\text{ K})/(400\text{ K}) = 0.25$.



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Carnot Cycle 4

- Can the efficiency of the Carnot engine reach 100%?
- To obtain 100% efficiency, T_{H} would have to be raised to infinity or T_{L} be lowered to absolute zero.
- Neither option is possible.
- The efficiency of a Carnot engine is always less than 100%.
- The total mechanical work from a Carnot cycle can be written as:

$$W = Q_{\mathrm{H}} - Q_{\mathrm{L}}$$

- Since $\varepsilon = W/Q_{\mathrm{H}}$, the efficiency of a Carnot engine is:

$$\varepsilon = \frac{Q_{\mathrm{H}} - U_{\mathrm{L}}}{Q_{\mathrm{H}}}$$

Carnot Cycle 5

- The efficiency of a Carnot engine is determined by the heat taken from the warmer reservoir minus the heat given back to the cooler reservoir.
- For this expression for the efficiency of a Carnot engine to yield an efficiency of 100%, the heat returned to the cooler reservoir would have to be zero.
- Conversely, if the efficiency of the Carnot engine is less than 100%, the engine cannot convert all the heat it takes in from the warmer reservoir to useful work.
- French physicist Nicolas Leonard Sadi Carnot (1796 to 1832), who developed the Carnot cycle in the 19th century, proved the following statement, known as **Carnot’s Theorem**.

Carnot Cycle 6

- Carnot's Theorem:

  No heat engine operating between two thermal reservoirs can be more efficient than a Carnot engine operating between the two thermal reservoirs.

- We can imagine running a Carnot engine in reverse, creating a "Carnot refrigerator."
- The maximum coefficient of performance for such a refrigerator operating between two thermal reservoirs is:

$$K_{\text{max}} = \frac{T_{\text{L}}}{T_{\text{H}} - T_{\text{L}}}$$

Carnot Cycle 7

- Similarly, the maximum coefficient of performance for a heat pump operating between two thermal reservoirs is:

$$K_{\text{heat pump max}} = \frac{T_{\mathrm{H}}}{T_{\mathrm{H}} - T_{\mathrm{L}}}$$

- Note that the Carnot cycle constitutes the ideal thermodynamic process, which is the absolute upper limit on what is theoretically attainable.
- Real-world complications lower the efficiency drastically, as we'll see.
- The typical coefficient of performance for a real refrigerator or heat pump is around 3.

Concept Check 4

- What is the maximum (Carnot) coefficient of performance of a refrigerator in a room with a temperature of 22.0 °C ?
- The temperature inside the refrigerator is kept at 2.0 °C.

A. 0.10

B. 0.44

C. 3.0

D. 5.8

E. 13.8

Solution Concept Check 4

- What is the maximum (Carnot) coefficient of performance of a refrigerator in a room with a temperature of 22.0 °C ?
- The temperature inside the refrigerator is kept at 2.0 °C.

A. 0.10

B. 0.44

C. 3.0

D. 5.8

[✓ E. 13.8]

$$K_{\mathrm{max}} = \frac{T_{\mathrm{L}}}{T_{\mathrm{H}} - T_{\mathrm{L}}}$$

$$K_{\mathrm{max}} = \frac{273\text{ K} + 2.0\text{ K}}{(273\text{ K} + 22.0\text{ K}) - (273\text{ K} + 2.0\text{ K})}$$

$$K_{\mathrm{max}} = 13.8$$

Concept Check 5

- What is the maximum (Carnot) coefficient of performance of a heat pump being used warm a house to an interior of temperature of 22.0 °C ?
- The temperature outside the house is 2.0 °C.

A. 0.15

B. 1.1

C. 3.5

D. 6.5

E. 14.8

Solution Concept Check 5

- What is the maximum (Carnot) coefficient of performance of a heat pump being used warm a house to an interior of temperature of 22.0 °C ?
- The temperature outside the house is 2.0 °C.

A. 0.15

B. 1.1

C. 3.5

D. 6.5

E. 14.8

$$K_{\text{max}} = \frac{T_{\text{H}}}{T_{\text{H}} - T_{\text{L}}}$$

$$K_{\text{max}} = \frac{273\text{ K} + 22.0\text{ K}}{(273\text{ K} + 22.0\text{ K}) - (273\text{ K} + 2.0\text{ K})}$$

$$K_{\text{max}} = 14.8$$

Work Done by a Carnot Engine 1

- A Carnot engine takes 3000 J of heat from a thermal reservoir with a temperature T_H = 500 K and discards heat to a thermal reservoir with a temperature T_L = 325 K.

PROBLEM:

- How much work does the Carnot engine do in this process

SOLUTION:

- Start with the definition of the efficiency of a heat engine:

$$\varepsilon = \frac{W}{Q_{\mathrm{H}}}$$

- The efficiency of a Carnot engine is:

$$\varepsilon = 1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$$

Work Done by a Carnot Engine 2

- Combining these two equations gives us:

$$\frac{W}{Q_{\mathrm{H}}} = 1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}$$

- The work done by the Carnot engine is:

$$W = Q_{\mathrm{H}}\left(1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}}\right)$$

- Putting in our numerical values gives us:

$$W = (3000\ \mathrm{J})\left(1 - \frac{325\ \mathrm{K}}{500\ \mathrm{K}}\right) = 1050\ \mathrm{J}$$

Maximum Efficiency of an Electric Power Plant 1

- Electricity can be generated by burning fossil fuels to produce steam, which in turn drives alternators that produce electricity.
- Power plants can produce steam with a temperature as high as 600. °C by pressurizing the steam.
- The resulting waste heat must be exhausted into the environment, which is at a temperature of 20.0 °C.

PROBLEM:

- What is the maximum efficiency of the power plant?

SOLUTION:

- The maximum efficiency of such a power plant is the efficiency of a Carnot heat engine.

Maximum Efficiency of an Electric Power Plant 2

- For a Carnot engine operating between 20.0 °C and 600. °C:

$$\varepsilon = 1 - \frac{T_{\mathrm{L}}}{T_{\mathrm{H}}} = 1 - \frac{293\ \mathrm{K}}{873\ \mathrm{K}} - 66.4\%$$

- Real power plants achieve a lower efficiency of around 40%.
- Many well-designed plants do not simply exhaust the waste heat into the environment.
- They employ cogeneration or combined heat and power (CHP).
- The heat that normally would be lost is used to heat nearby buildings or houses.
- This heat can even be used to operate air conditioners that cool nearby structures, a process called trigeneration.

Cost to Operate an Electric Power Plant 1

- An electric power plant operates steam turbines at a temperature of 557 °C and uses cooling towers to keep the cooler thermal reservoir at a temperature of 38.3 °C.
- The operating cost of the plant for 1 yr is $52.0 million.
- The managers propose using the water from a nearby lake to lower the temperature of the cooler reservoir to 8.90 °C.
- Assume that the plant operates at maximum possible efficiency.

PROBLEM:

- How much will the operating cost of the plant be reduced in 1 yr because of the change in reservoir temperature?
- Assume that the plant generates the same amount of electricity.

Cost to Operate an Electric Power Plant 2

SOLUTION:

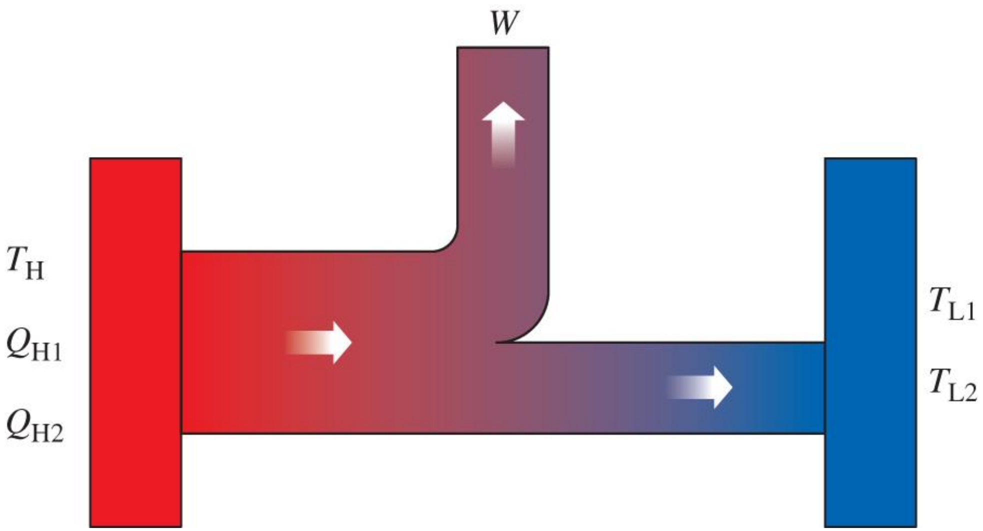
Think

- We can calculate the efficiency of the power plant if it operates at the theoretical Carnot efficiency, which depends only on the temperatures of the warmer thermal reservoir and the cooler thermal reservoir.
- We can calculate the amount of thermal energy put into the warmer reservoir and assume that the cost of operating the plant is proportional to that thermal energy.
- This thermal energy might come from the burning of fuel (coal, oil, or gas) or perhaps from a nuclear reactor.

Cost to Operate an Electric Power Plant 3

- Lowering the temperature of the cooler reservoir will increase the efficiency of the power plant and lower the required amount of thermal energy and the associated cost.
- The cost savings are then the operating cost of the original plant minus the operating cost of the improved plant.

Sketch



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Cost to Operate an Electric Power Plant 4

Research

- The maximum efficiency of the power plant when operating with the cooling towers is given by the Carnot efficiency:

$$\varepsilon_1 = \frac{T_{\mathrm{H}} - T_{\mathrm{L1}}}{T_{\mathrm{H}}}$$

- The efficiency of the power plant under this condition can also be expressed as:

$$\varepsilon_1 = \frac{W}{Q_{\mathrm{H1}}}$$

- When the lake is used, we have:

$$\varepsilon_2 = \frac{T_{\mathrm{H}} - T_{\mathrm{L2}}}{T_{\mathrm{H}}} \text{ and } \varepsilon_2 = \frac{W}{Q_{\mathrm{H2}}}$$

Cost to Operate an Electric Power Plant 5

- The cost to operate the power plant is proportional to the thermal energy supplied to the warmer reservoir.
- We can thus equate the ratio of the original cost, c_1, to the lowered cost, c_2, with the ratio of the thermal energy originally required, Q_{H1}, to the thermal energy subsequently required, Q_{H2}:

$$\frac{c_1}{c_2} = \frac{Q_{\mathrm{H1}}}{Q_{\mathrm{H2}}}$$

Simplify

- The new cost is:

$$c_2 = c_1 \frac{Q_{\mathrm{H2}}}{Q_{\mathrm{H1}}}$$

Cost to Operate an Electric Power Plant 6

- Putting our first two equations together gives us the thermal energy originally required:

$$Q_{\mathrm{H1}} = \frac{W}{\varepsilon_1} = \frac{W}{\dfrac{T_{\mathrm{H}} - T_{\mathrm{L1}}}{T_{\mathrm{H}}}} = \frac{T_{\mathrm{H}} W}{T_{\mathrm{H}} - T_{\mathrm{L1}}}$$

- The thermal energy required using the lake is:

$$Q_{\mathrm{H1}} = \frac{W}{\varepsilon_2} = \frac{W}{\dfrac{T_{\mathrm{H}} - T_{\mathrm{L2}}}{T_{\mathrm{H}}}} = \frac{T_{\mathrm{H}} W}{T_{\mathrm{H}} - T_{\mathrm{L2}}}$$

Cost to Operate an Electric Power Plant 7

- The new cost is:

$$c_2 = c_1 \frac{Q_{\mathrm{H}2}}{Q_{\mathrm{H}1}} = c_1 \frac{\dfrac{T_{\mathrm{H}} W}{T_{\mathrm{H}} - T_{\mathrm{L}2}}}{\dfrac{T_{\mathrm{H}} W}{T_{\mathrm{H}} - T_{\mathrm{L}1}}} = c_1 \frac{T_{\mathrm{H}} - T_{\mathrm{L}1}}{T_{\mathrm{H}} - T_{\mathrm{L}2}}$$

- The work done by the power plant cancels out because the plant generates the same amount of electricity in both cases.
- The cost savings are:

$$c_1 - c_2 = c_1 - c_1 \frac{T_{\mathrm{H}} - T_{\mathrm{L}1}}{T_{\mathrm{H}} - T_{\mathrm{L}2}} = c_1 \left(1 - \frac{T_{\mathrm{H}} - T_{\mathrm{L}1}}{T_{\mathrm{H}} - T_{\mathrm{L}2}}\right) = c_1 \frac{T_{\mathrm{L}1} - T_{\mathrm{L}2}}{T_{\mathrm{H}} - T_{\mathrm{L}2}}$$

Cost to Operate an Electric Power Plant 8

Calculate

- Putting in our numerical values:

$$c_1 - c_2 = c_1 \frac{T_{\text{L1}} - T_{\text{L2}}}{T_{\text{H}} - T_{\text{L2}}} = (\$52.0 \text{ million}) \frac{311.45 \text{ K} - 282.05 \text{ K}}{830.15 \text{ K} - 282.05 \text{ K}}$$

$$c_1 - c_2 = \$2.78927 \text{ million}$$

Round

- We report our result to three significant figures:

$$c_1 - c_2 = \$2.79 \text{ million}$$

Double-check

- To double-check our result, we calculate the efficiency of the power plant using cooling towers and using the lake.

Cost to Operate an Electric Power Plant 9

- Using the cooling towers we get:

$$\varepsilon_1 = \frac{T_\mathrm{H} - T_\mathrm{L1}}{T_\mathrm{H}} = \frac{830.15\ \mathrm{K} - 311.4\ \mathrm{K}}{830.15\ \mathrm{K}} = 62.5\%$$

- Using the lake we get:

$$\varepsilon_2 = \frac{T_\mathrm{H} - T_\mathrm{L2}}{T_\mathrm{H}} = \frac{830.15\ \mathrm{K} - 282.05\ \mathrm{K}}{830.15\ \mathrm{K}} = 66.0\%$$

- Using the lake provides higher efficiency, which seems reasonable.
- To check further, we verify that the ratio of the two efficiencies is equal to the inverse of the ratio of the two costs, because a higher efficiency means a lower cost.

Cost to Operate an Electric Power Plant 10

- The ratio of the two efficiencies is:

$$\frac{\varepsilon_1}{\varepsilon_2} = \frac{62.5\%}{66.7\%} = 0.947$$

- The inverse ratio of the two costs is:

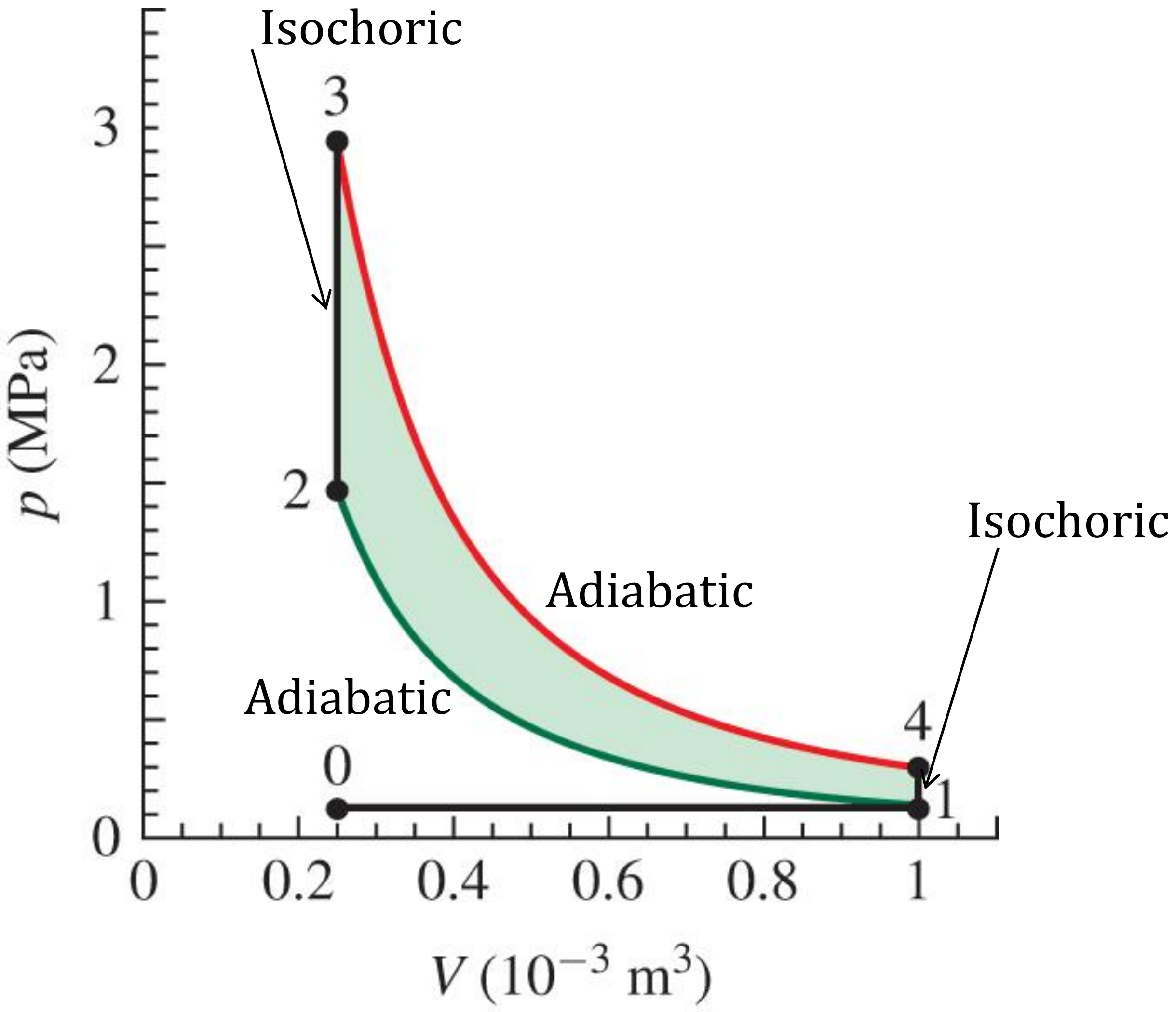
$$\frac{c_2}{c_1} = \frac{\$52\text{ million} - \$2.79\text{ million}}{\$52\text{ million}} = 0.946$$

- These ratios agree with rounding errors, so our result seems reasonable.

Otto Cycle 1

- A real heat engine based on the Carnot cycle is not practical.
- However, many practical heat engines that are in everyday use are designed to operate via cyclical thermodynamic processes.
- For an example of the operation of a real-world engine, let’s examine the Otto cycle.
- Again, we assume an ideal gas as the working medium.
- The **Otto cycle** is used in the modern internal combustion engines inside automobiles.
- This cycle consists of two adiabatic processes and two constant-volume processes and is the default configuration for a four-cycle internal combustion engine.

Otto Cycle 2



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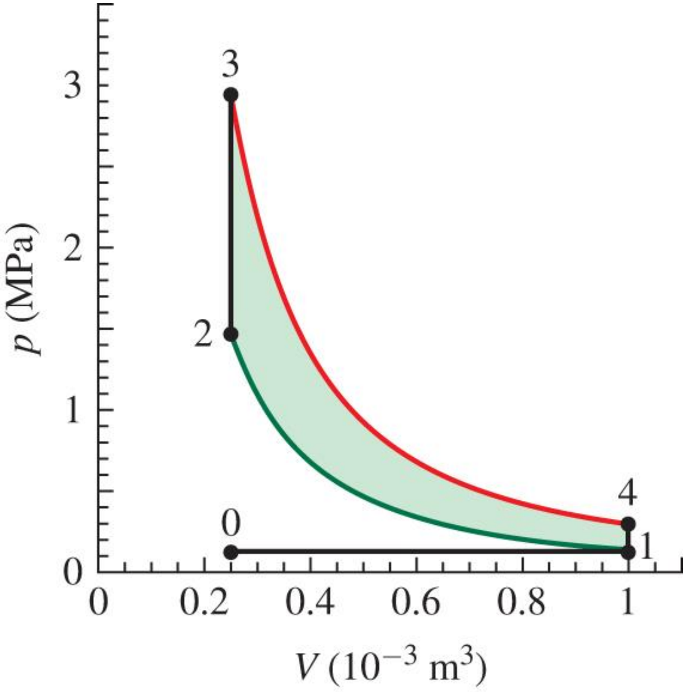
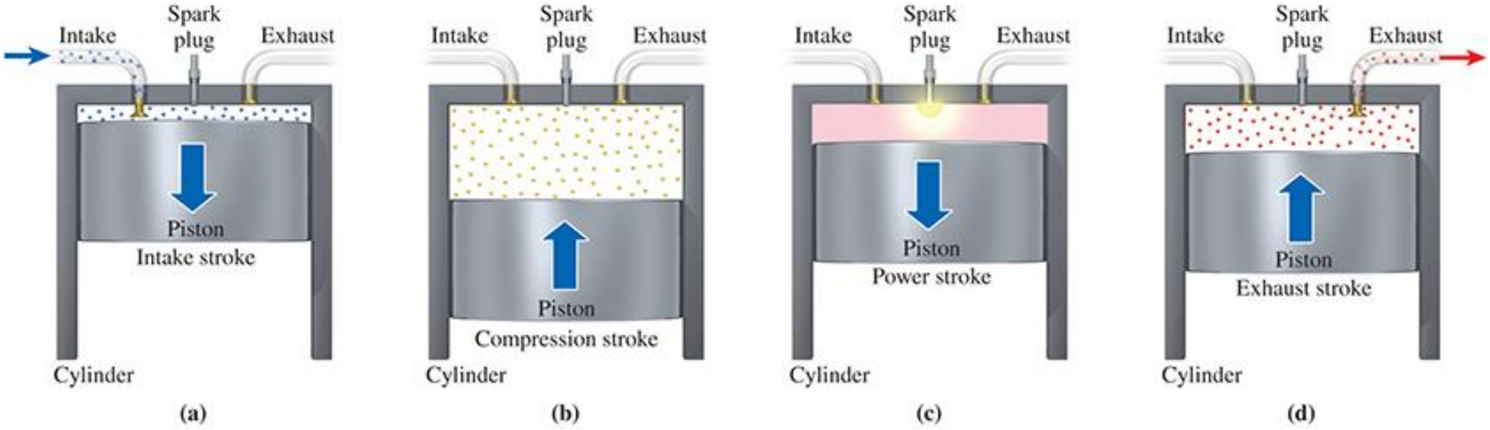
Otto Cycle 3

- Intake stroke: 0 to 1
- Intake valve closes at 1
- Compression stroke: 1 to 2
- Fuel-air ignition: 2 to 3
- Power stroke: 3 to 4
- Exhaust valve opens at 4; 4 to 1
- Exhaust stroke: 1 to 0





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Otto Cycle 4

- The ratio of the expanded volume, V_1, to the compressed volume, V_2 , is called the *compression ratio*:

$$r = \frac{V_1}{V_2}$$

- The efficiency of the Otto cycle can be expressed as a function of the compression ratio only (Deriv. 20.2):

$$\varepsilon = 1 - r^{1-\gamma}$$

- Here are two examples:

$$r = 10.7 \;\Rightarrow\; \varepsilon = 61.3\% \qquad r = 9.50 \;\Rightarrow\; \varepsilon = 59.4\%$$

- In contrast, for the Carnot cycle, the efficiency depends only on the ratio of two temperatures.

Otto Cycle 5

- Note, however, that this is the theoretical upper limit for the efficiency at this compression ratio.
- In principle, an internal combustion engine can be made more efficient by increasing the compression ratio, but practical factors prevent that approach.
- For example, if the compression ratio is too high, the fuel-air mixture will detonate before the compression is complete.
- Very high compression ratios put high stresses on the components of the engine.
- The actual compression ratios of gasoline-powered internal combustion engines range from 8 to 12.

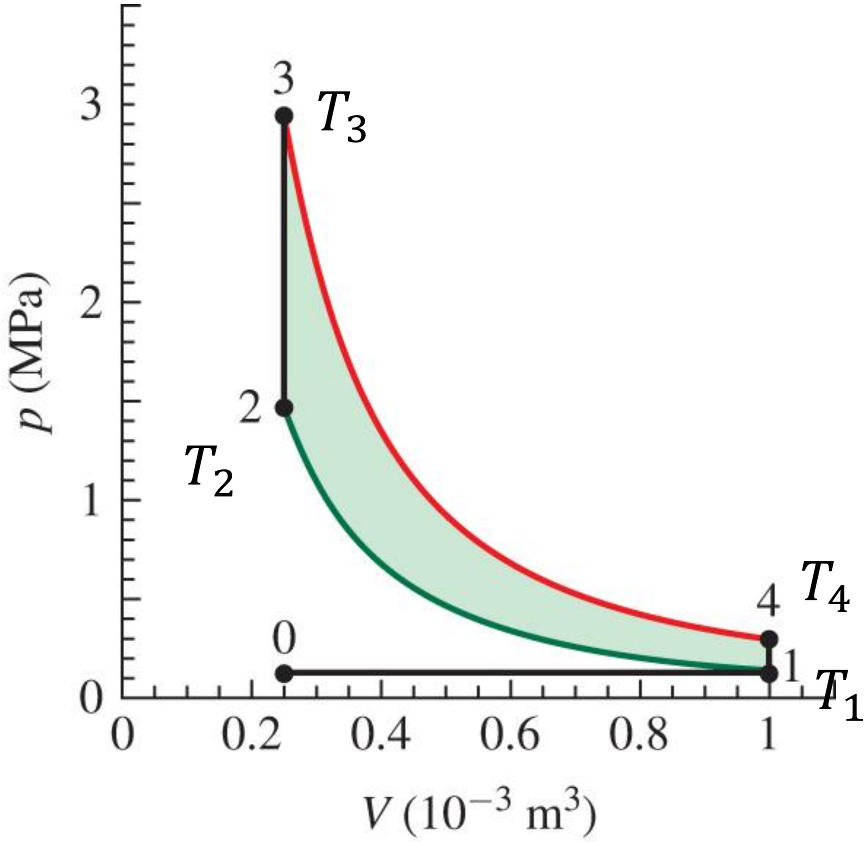
Real Otto Engines

- The actual efficiency of an internal combustion engine is about 20%.
- Why is this so much lower than the theoretical upper limit?
- First, the "adiabatic" parts of the cycle do not really proceed without heat exchange between the gas in the piston and the engine block.
- Second, the gasoline-air mixture is not quite an ideal gas.
- Third, during the ignition and heat rejection processes, the volume does not stay exactly constant, because both processes take some time.
- Fourth, during the intake and exhaust strokes, the pressure in the chamber is not exactly atmospheric pressure because of gas dynamics considerations.

Concept Check 6

- Which of the four temperatures in the Otto cycle is the highest?

A. T_1
B. T_2
C. T_3
D. T_4
E. All four are identical.



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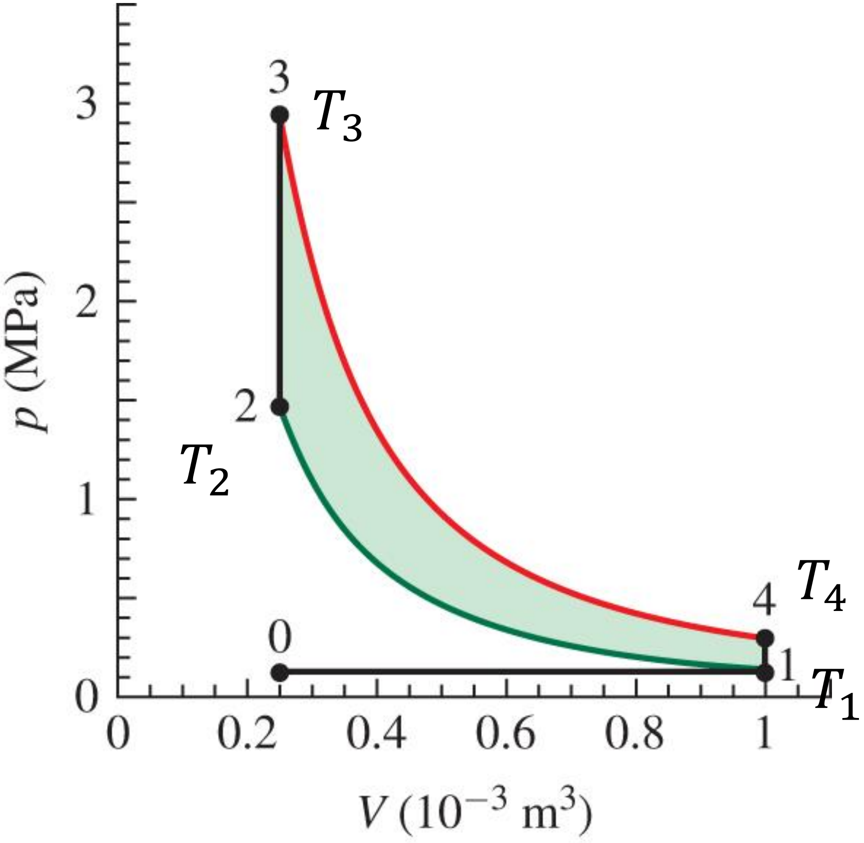
Solution Concept Check 6

- Which of the four temperatures in the Otto cycle is the highest?

A. T_1
B. T_2
C. T_3
D. T_4
E. All four are identical.



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Efficiency of an Automobile Engine 1

- A car with a gasoline-powered internal combustion engine travels with a speed of 26.8 m/s (60.0 mph) on a level road and uses gas at a rate of 6.92 L/100 km (34.0 mpg).
- The energy content of gasoline is 34.8 MJ/L.

PROBLEM:

- If the engine has an efficiency of 20.0%, how much power is delivered to keep the car moving at a constant speed?

SOLUTION:

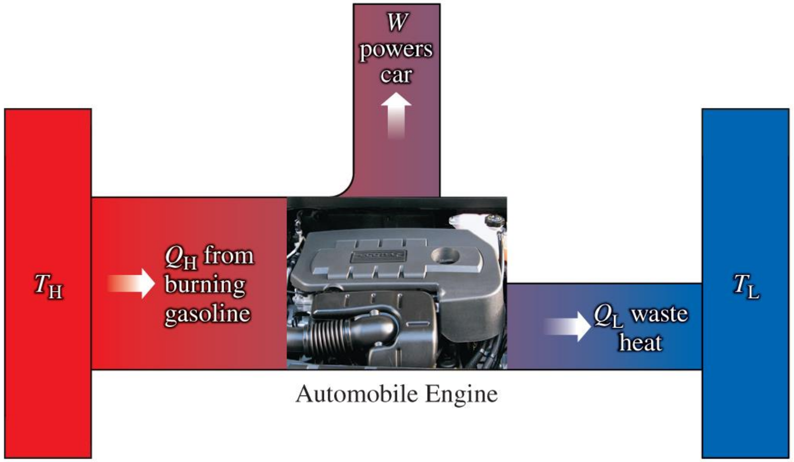
Think

- We can calculate how much energy is being supplied to the engine by calculating the amount of fuel used and multiplying by the energy content of that fuel.

Efficiency of an Automobile Engine 2

- The efficiency is the useful work divided by the energy being supplied.
- Once we determine the energy supplied, we can find the useful work from the given efficiency of the engine.
- By dividing the work and the energy by an arbitrary time interval, we can determine the average power delivered.

Sketch



W. Bauer and G. D. Westfall

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Efficiency of an Automobile Engine 3

Research

- The car is traveling at speed v.
- The rate at which the car burns gasoline can be expressed in terms of the volume of gasoline burned per unit distance.
- We can calculate the volume of gasoline burned per unit time, V_t, by multiplying the speed of the car by the rate at which the car burns gasoline:

$$V_{\mathrm{t}} = \chi v$$

- The energy per unit time supplied to the engine by consuming fuel is the power, P, given by the volume of gasoline used per unit time multiplied by the energy content of gasoline, E_g:

$$P = V_{\mathrm{t}} E_{\mathrm{g}}$$

Efficiency of an Automobile Engine 4

- The efficiency of the engine is given by:

$$\varepsilon = \frac{W}{Q_{\mathrm{H}}}$$

- Here W is the useful work and Q_{H} is the thermal energy supplied to the engine.
- If we divide both W and Q_{H} by a time interval, t, we get:

$$\varepsilon = \frac{W/t}{Q_{\mathrm{H}}/t} = \frac{P_{\mathrm{delivered}}}{P}$$

Simplify

- Combining our equations gives us:

$$P_{\mathrm{delivered}} = \varepsilon P = \varepsilon V_{\mathrm{t}} E_{\mathrm{g}} = \varepsilon \chi v E_{\mathrm{g}}$$

Efficiency of an Automobile Engine 5

Calculate

- The power delivered is:

$$P_{\text{delivered}} = \varepsilon\chi v E_{\text{g}} = (0.200)\frac{6.92\ \text{L}}{100 \cdot 10^3\ \text{m}}(26.3\ \text{m/s})(34.8 \cdot 10^6\ \text{J/L})$$

$$P_{\text{delivered}} = 12{,}907.7\ \text{W}$$

Round

- We report our result to three significant figures:

$$P_{\text{delivered}} = 12.9\ \text{kW} = 17.3\ \text{hp}$$

Double-check

- To double-check our result, we calculate the power required to keep the car moving at 60.0 mph against air resistance.

Efficiency of an Automobile Engine 6

- The power required, P_{air}, is equal to the product of the force of air resistance, F_{drag}, and the speed of the car:

$$P_{\text{air}} = F_{\text{drag}} v$$

- The drag force created by air resistance is given by:

$$F_{\text{drag}} = K v^2$$

- The constant K has been found empirically to be:

$$K = \frac{1}{2} c_{\text{d}} A \rho$$

- Here c_{d} is the drag coefficient of the car, A is its front cross-sectional area, and ρ is the density of air.

Efficiency of an Automobile Engine 7

- Combining our equations gives us:

$$P_{\text{air}} = F_{\text{drag}}v = (Kv^2)v = \frac{1}{2}c_{\text{d}}A\rho v^3$$

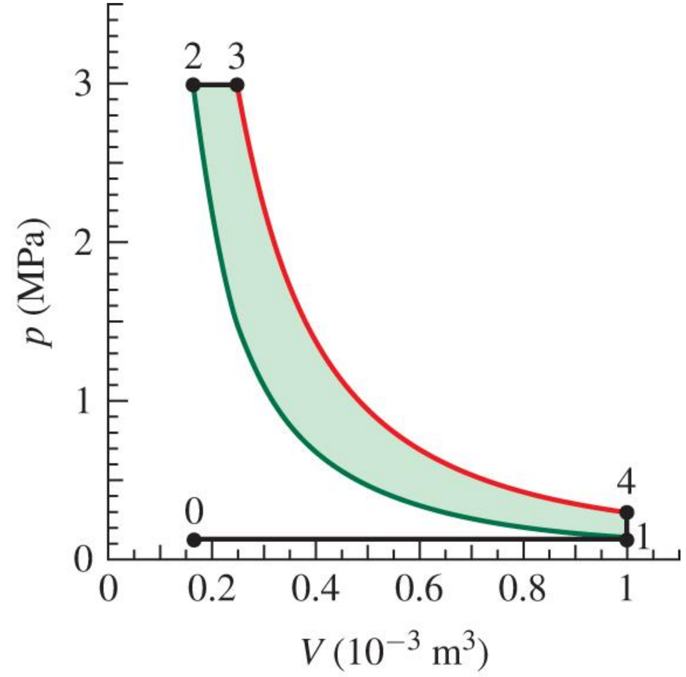
- Using $c_{\text{d}} = 0.33$, $A = 2.2\ \text{m}^2$, and $\rho = 1.29\ \text{kg/m}^3$, we get:

$$P_{\text{air}} = \frac{1}{2}(0.33)(2.2\ \text{m}^2)(1.29\ \text{kg/m}^3)(26.8\ \text{m/s})^3 = 9014\ \text{W} = 9.0\ \text{kW}$$

- The power required to overcome air resistance ($P_{\text{air}} = 9.0$ kW = 12 hp) is about 70% of the calculated value for the power delivered ($P_{\text{delivered}} = 12.9$ kW = 17.3 hp).
- The remaining power is used to overcome other kinds of friction, such as rolling friction.
- Thus, our answer seems reasonable.

Diesel Cycle 1

- Diesel engines and gasoline engines have somewhat different designs.
- Diesel engines do not compress a fuel-air mixture, but rather air only (path from point 1 to point 2, green curve).
- The fuel is introduced (between point 2 and point 3) only after the air has been compressed.
- The thermal energy from the compression ignites the mixture (thus, no spark plug is required).
- This combustion process pushes the piston out at constant pressure.



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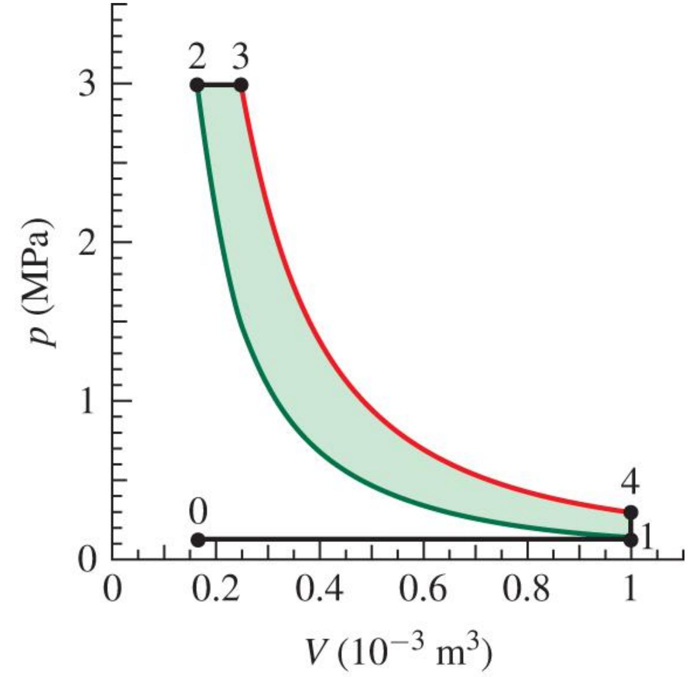
Diesel Cycle 2

- After combustion, the combustion products push the piston out farther in the same adiabatic manner as in the Otto cycle (path from point 3 to point 4, red curve).
- The process of heat rejection to the environment at constant volume (between points 4 and 1 in the diagram) also proceeds in the same way as in the Otto cycle, as do the intake stroke (path from 0 to 1) and exhaust stroke (path from 1 to 0).



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Diesel Cycle 3

- Diesel engines have a higher compression ratio and thus a higher efficiency than gasoline-powered four-stroke engines, although they have a slightly different thermodynamic cycle.
- The efficiency of an ideal diesel engine is given by:

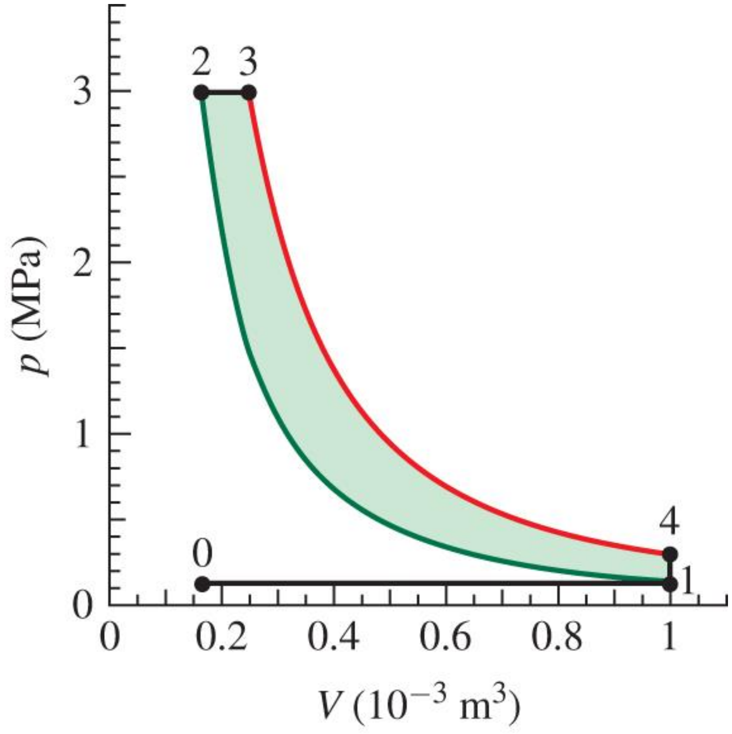
$$\varepsilon = 1 - r^{1-\gamma}\frac{\alpha^{\gamma} - 1}{\gamma(\alpha - 1)}$$

- Here α is the *cut-off ratio* between the final and initial volumes of the combustion phase.

Concept Check 7

- In which part of the Diesel cycle is heat added?

A. on the path from point 0 to point 1
B. on the path from point 1 to point 2
C. on the path from point 2 to point 3
D. on the path from point 3 to point 4
E. on the path from point 4 to point 1



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Solution Concept Check 7

- In which part of the Diesel cycle is heat added?

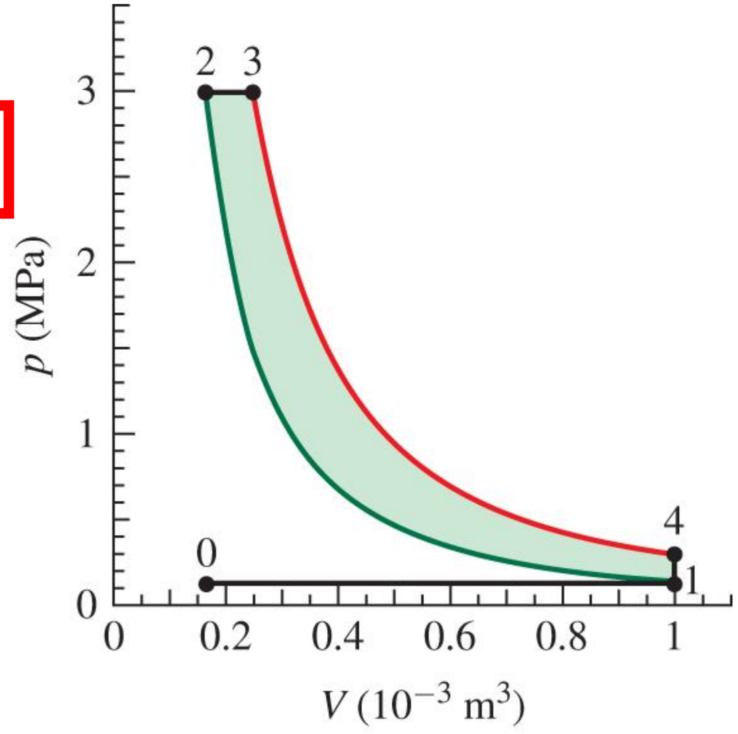
A. on the path from point 0 to point 1

B. on the path from point 1 to point 2

C. on the path from point 2 to point 3

D. on the path from point 3 to point 4

E. on the path from point 4 to point 1



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Concept Check 8

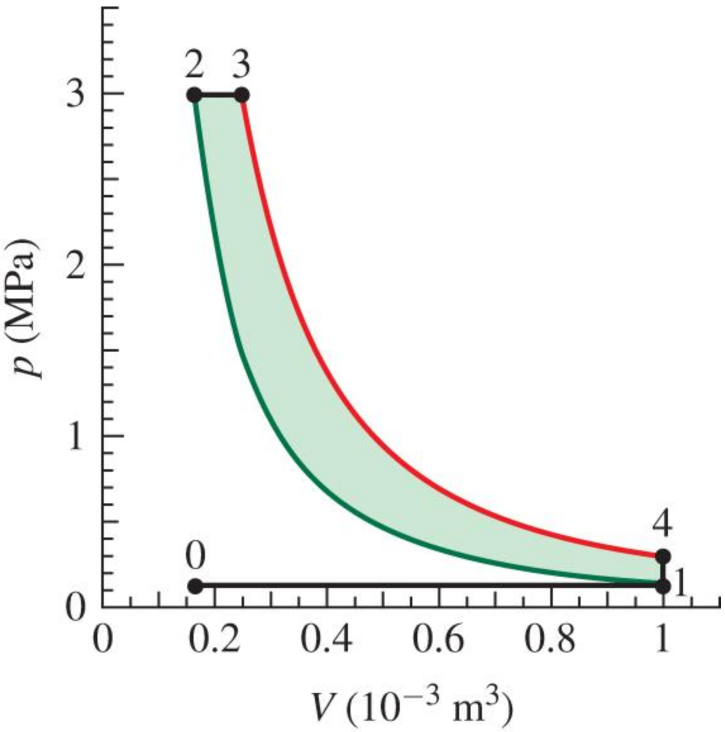
- During which part(s) of the Diesel cycle is mechanical work done by the engine?

A. on the path from point 0 to point 1 and on the path from point 1 to point 0

B. on the path from point 1 to point 2

C. on the path from point 2 to point 3 and on the path from point 3 to point 4

D. on the path from point 4 to point 1



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Solution Concept Check 8

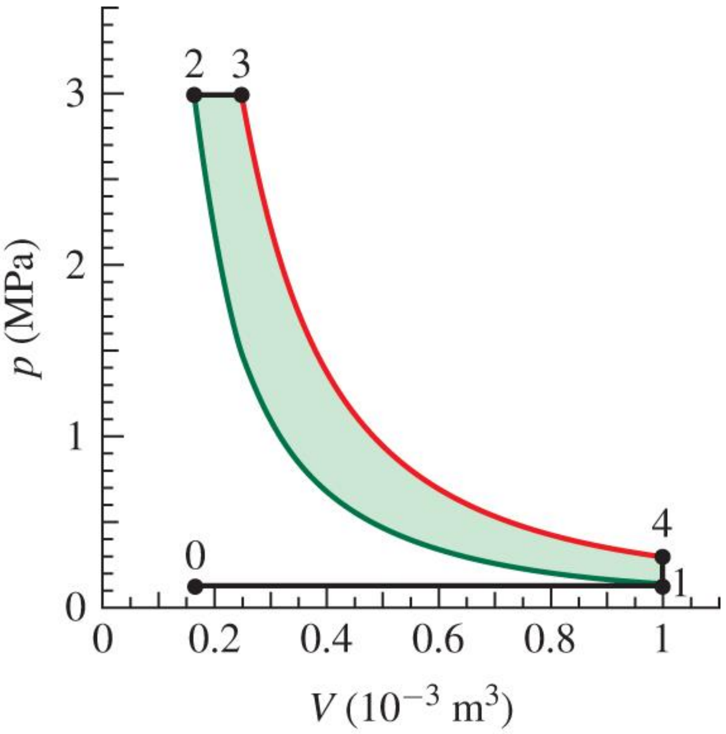
- During which part(s) of the Diesel cycle is mechanical work done by the engine?

A. on the path from point 0 to point 1 and on the path from point 1 to point 0

B. on the path from point 1 to point 2

C. on the path from point 2 to point 3 and on the path from point 3 to point 4

D. on the path from point 4 to point 1



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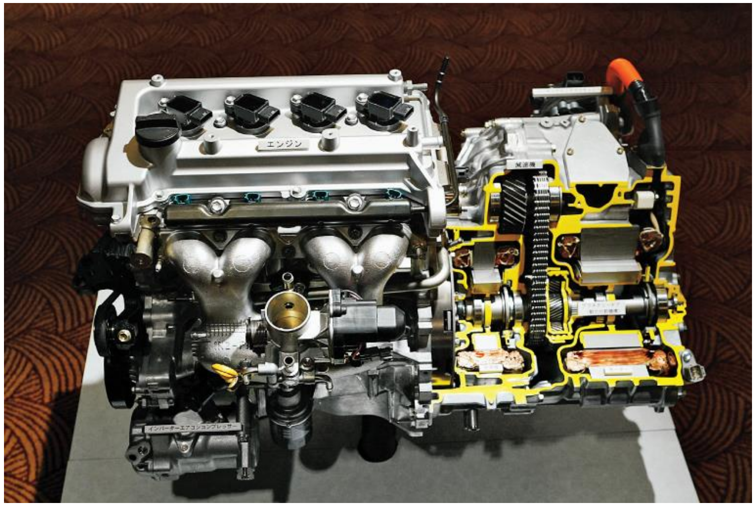
Hybrid Cars

- Hybrid cars combine a gasoline engine and an electric motor to achieve higher efficiency than a gasoline engine alone can achieve.
- The improvement in efficiency results from using a smaller gasoline engine than would normally be necessary and an electric motor, run off a battery charged by the gasoline engine, to supplement the gasoline engine when higher power is required.
- The Ford Escape Hybrid has a 114-kW (153-hp) gasoline engine coupled with a 70-kW (94-hp) electric motor, and the Ford Escape has a 128-kW (171-hp) gasoline engine.



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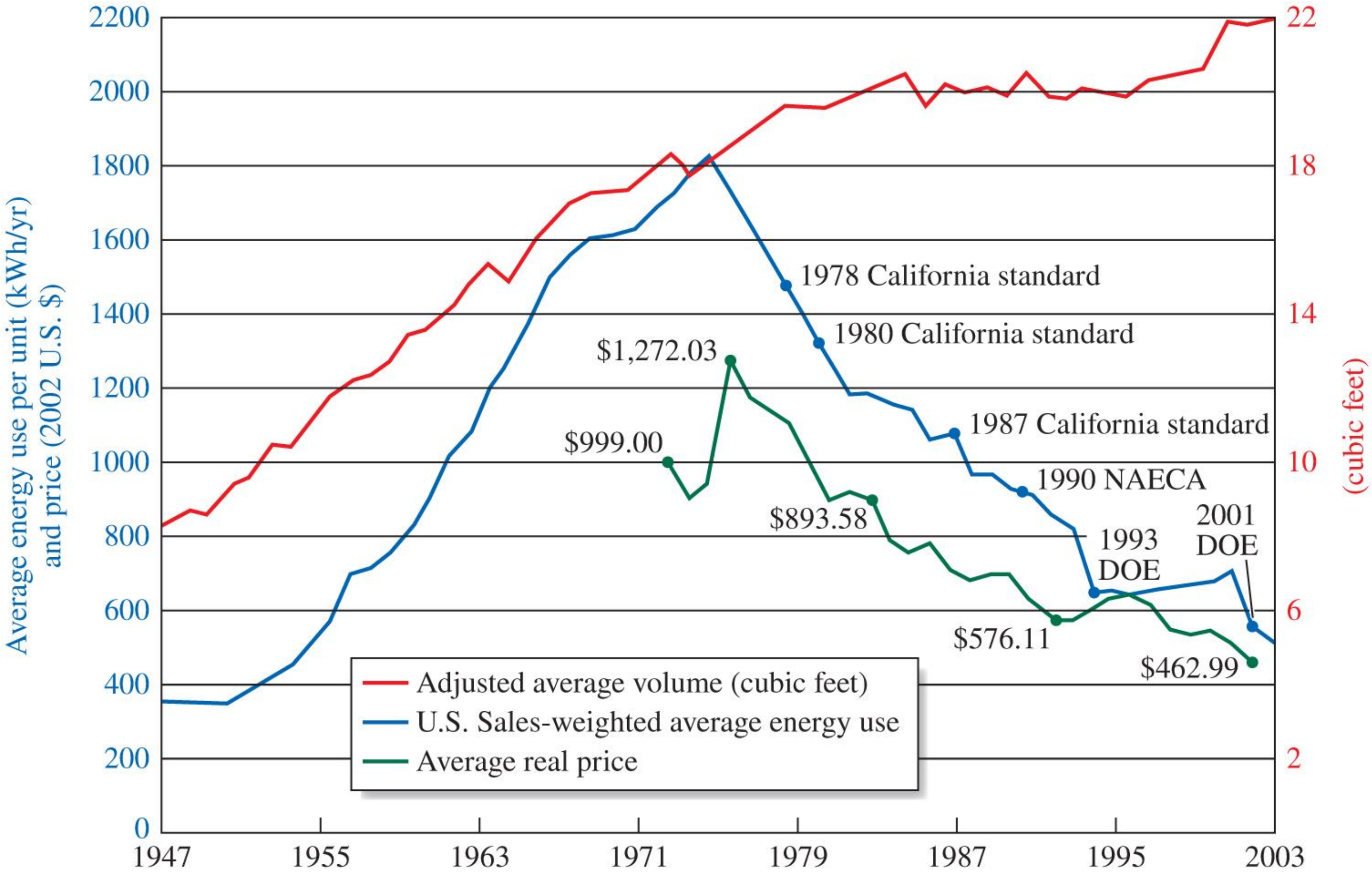
Efficiency and the Energy Crisis 1

- The efficiencies of engines and refrigerators have important economic consequences, which are relevant to solving the energy crisis.
- The efficiencies and performance coefficients calculated in this chapter with the aid of thermodynamic principles are theoretical upper limits.
- Real-world complications reduce the actual efficiencies of engines and performance coefficients of refrigerators.
- Engineering research can overcome these real-world complications and provide better performance of real devices, approaching the ideal limits.
- One impressive example of performance improvement has occurred with refrigerators sold in the United States, according to data compiled by Steve Chu.

Efficiency and the Energy Crisis 2



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Efficiency and the Energy Crisis 3

- Between 1975 and 2003, the average size of a refrigerator in U.S. kitchens increased by about 20%, but through a combination of tougher energy standards and research and development on refrigerator design and technology, the average power consumption fell by two-thirds, a total of 1200 kWh/yr, from 1800 kWh/yr in 1975 to 600 kWh/yr in 2003.
- Since about 150 million new refrigerators and freezers are purchased each year in the US, and each one saves approximately 1200 kWh/yr, a total energy savings of 180 billion kWh ($6.5 \cdot 10^{17}$ J = 0.65 EJ) is realized each year.
- In 2009, this savings was approximately twice as much as the combined energy produced using wind power, solar energy, geothermal, and biomass.

Freezing Water in a Refrigerator 1

- Suppose we have 250 g of water at 0.00 °C.
- We want to freeze this water by putting it in a refrigerator operating in a room with a temperature of 22.0 °C.
- The temperature inside the refrigerator is −5.00 °C.

PROBLEM:

- What is the minimum amount of electrical energy that must be supplied to the refrigerator to freeze the water?

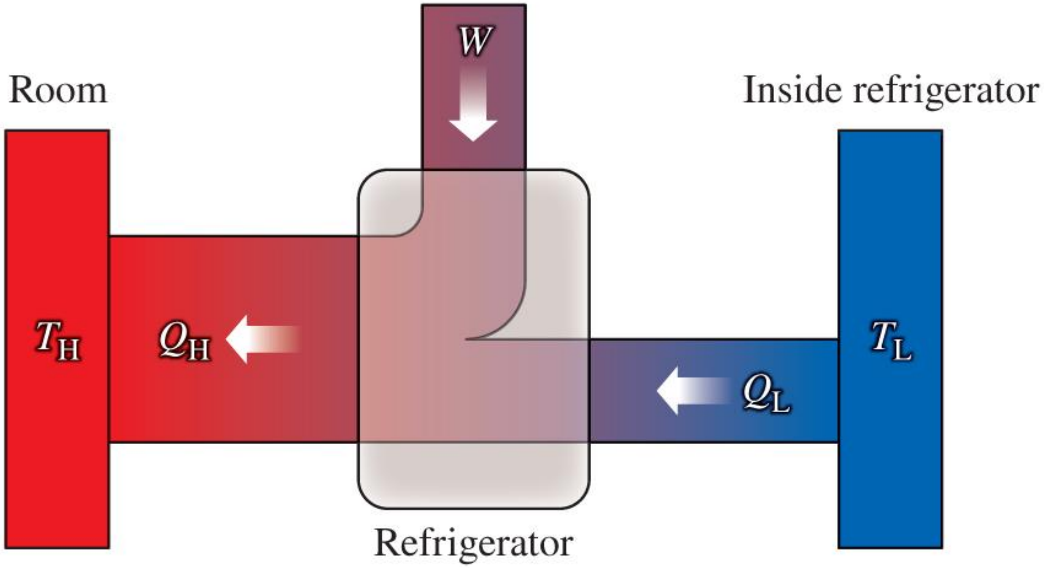
SOLUTION:

Think

- The amount of heat that must be removed depends on the latent heat of fusion and the given mass of water.

Freezing Water in a Refrigerator 2

- The most efficient refrigerator possible is a Carnot refrigerator, so we will use the theoretical maximum coefficient of performance.
- Knowing the amount of heat to be removed from the low-temperature reservoir and the coefficient of performance, we can calculate the minimum energy that must be supplied.
- **Sketch**



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Freezing Water in a Refrigerator 3

Research

- The most efficient refrigerator possible is a Carnot refrigerator.
- The maximum coefficient of performance of a Carnot refrigerator is given by:

$$K_{\text{max}} = \frac{Q_{\text{L}}}{W} = \frac{T_{\text{L}}}{T_{\text{H}} - T_{\text{L}}}$$

- Here Q_{L} is the heat removed from inside the refrigerator, W is the work (in terms of electrical energy) that must be supplied, T_{L} is the temperature inside the refrigerator, and T_{H} is the temperature of the room.

Freezing Water in a Refrigerator 4

- The amount of heat that must be removed to freeze a mass *m* of water is given by:

$$Q_{\mathrm{L}} = mL_{\mathrm{fusion}}$$

- Here $L_{\mathrm{fusion}} = 334$ kJ/kg is the latent heat of fusion of water.

Simplify

- We can solve our first equation for the energy that must be supplied to the refrigerator:

$$W = Q_{\mathrm{L}} \frac{T_{\mathrm{H}} - T_{\mathrm{L}}}{T_{\mathrm{L}}}$$

- Substituting in the heat removed gives us:

$$W = (mL_{\mathrm{fusion}}) \frac{T_{\mathrm{H}} - T_{\mathrm{L}}}{T_{\mathrm{L}}}$$

Freezing Water in a Refrigerator 5

Calculate

- Putting in our numerical values gives us:

$$W = (mL_{\text{fusion}})\frac{T_{\text{H}} - T_{\text{L}}}{T_{\text{L}}}$$

$$W = (0.250\ \text{kg})(334\ \text{kJ/kg})\frac{295.15\ \text{K} - 268.15\ \text{K}}{268.15\ \text{K}} = 8.41231\ \text{J}$$

Round

- We report our result to three significant figures:

$$W = 8.41\ \text{J}$$

Double-check

- Let's calculate the heat removed from the water:

$$Q_{\text{L}} = mL_{\text{fusion}} = (0.250\ \text{kg})(334\ \text{kg/kJ}) = 83.5\ \text{kJ}$$

Freezing Water in a Refrigerator 6

- Using our result for the energy required to freeze the water, we can calculate the coefficient of performance of the refrigerator:

$$K = \frac{Q_\mathrm{L}}{W} = \frac{83.5\ \mathrm{kJ}}{8.41\ \mathrm{kJ}} = 9.93$$

- The maximum coefficient of performance of a Carnot refrigerator is:

$$K_\mathrm{max} = \frac{T_\mathrm{L}}{T_\mathrm{H} - T_\mathrm{L}} = \frac{268.15\ \mathrm{K}}{295.15\ \mathrm{K} - 268.15\ \mathrm{K}} = 9.93$$

- Our results seem reasonable.
- Note the relatively large amount of energy required by a refrigerator to freeze a small quantity of water.

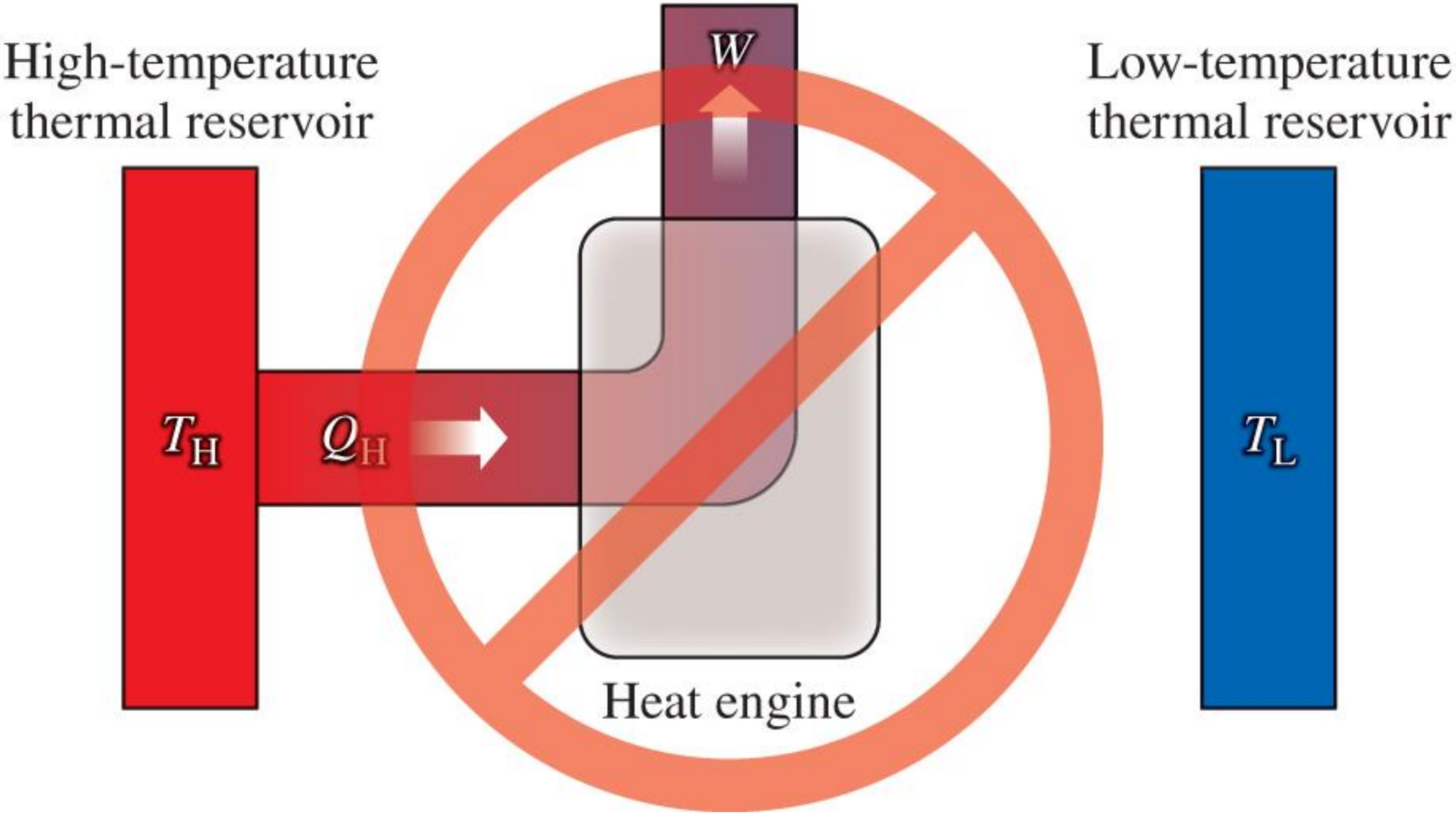
The Second Law of Thermodynamics 1

- It is not possible to construct a 100% efficient heat engine.
- This fact forms the basis of the
  Second Law of Thermodynamics:

  It is impossible for a system to undergo a process in which it absorbs heat from a thermal reservoir at a given temperature and converts that heat completely to mechanical work without rejecting heat to a thermal reservoir at a lower temperature.

- This formulation is often called the *Kelvin–Planck statement of the Second Law of Thermodynamics*.

The Second Law of Thermodynamics 2



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The Second Law of Thermodynamics 3

- As an example, consider a book sliding on a table.
- The book slides to a stop, and the mechanical energy of motion is turned into thermal energy.
- This thermal energy takes the form of random motion of the molecules of the book, the air, and the table.
- It is impossible to convert this random motion back into organized motion of the book.
- It is, however, possible to convert some of the random motion related to thermal energy back into mechanical energy.
- Heat engines do that kind of conversion.

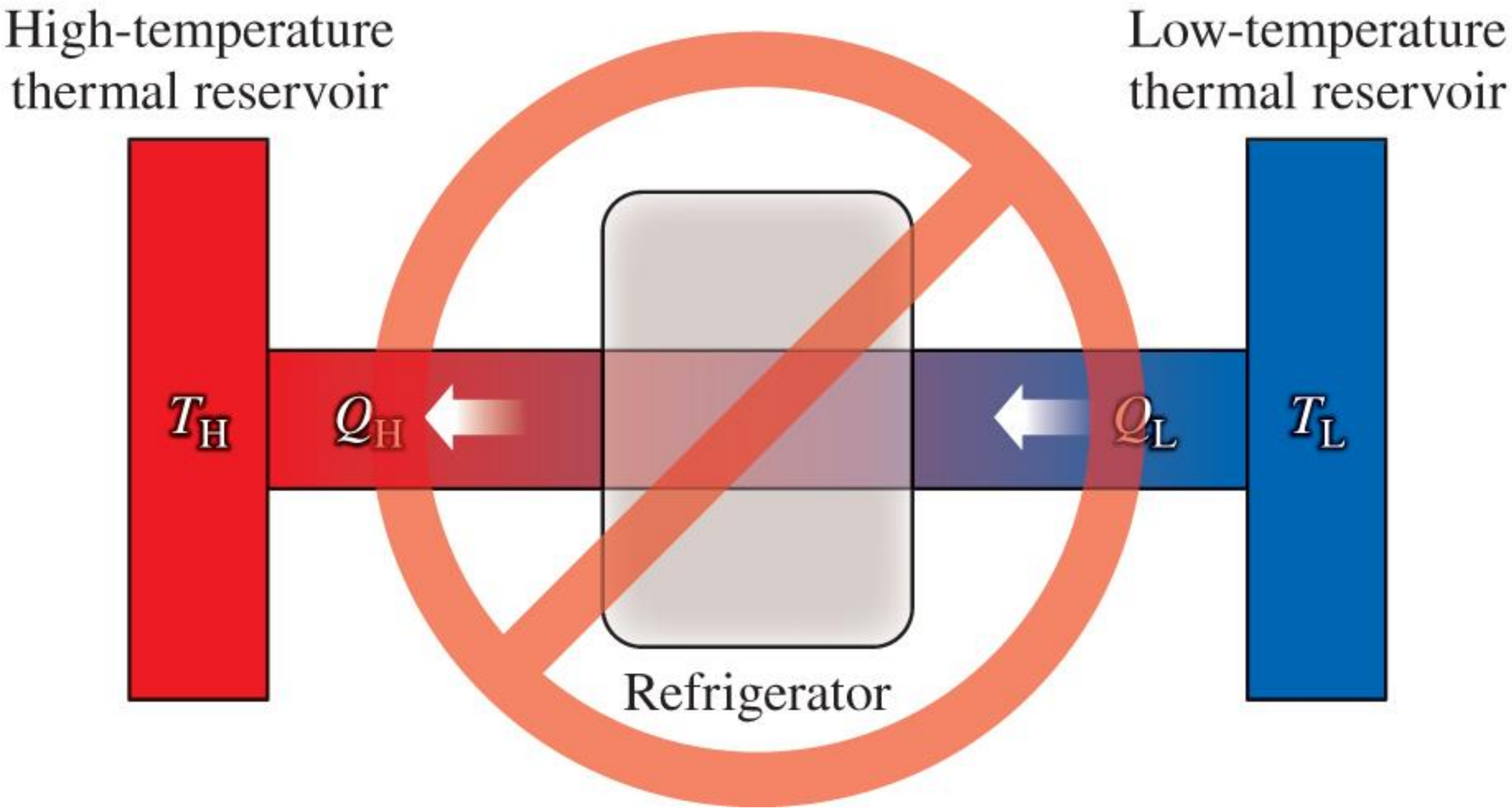
The Second Law of Thermodynamics 4

- If the Second Law were not true, various impossible scenarios could occur.
- For example, an electric power plant could operate by taking heat from the surrounding air, and an ocean liner could power itself by taking heat from the seawater.
- These scenarios do not violate the First Law of Thermodynamics because energy is conserved.
- The fact that they cannot occur shows that the Second Law contains additional information about how nature works, beyond the principle of conservation of energy.
- The Second Law limits the ways in which energy can be used.

The Second Law of Thermodynamics 5

- Another way to state the Second Law relates to refrigerators.
- We know that heat flows spontaneously from a warmer thermal reservoir to a cooler thermal reservoir.
- Heat never spontaneously flows from a cooler thermal reservoir to a warmer thermal reservoir.
- A refrigerator is a heat engine that moves heat from a cooler thermal reservoir to a warmer thermal reservoir; however, energy has to be supplied to the refrigerator for this transfer to take place.

The Second Law of Thermodynamics 6



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The Second Law of Thermodynamics 7

- The fact that it is impossible for a refrigerator to transfer thermal energy from a cooler reservoir to a warmer reservoir without using work is the basis of another form of the Second Law of Thermodynamics:

  It is impossible for any process to transfer thermal energy from a cooler thermal reservoir to a warmer thermal reservoir without any work having been done to accomplish the transfer.

- This equivalent formulation is often called the *Clausius statement of the Second Law of Thermodynamics*.

Entropy 1

- We have stated the Second Law of Thermodynamics somewhat differently from other laws such as Newton's laws, because we phrased it in terms of impossibilities.
- The Second Law can be stated in a more direct manner using the concept of **entropy**.
- If two objects at different temperatures are brought into thermal contact, both of their temperatures will asymptotically approach a common equilibrium temperature.
- What drives this system to thermal equilibrium is entropy, and the state of thermal equilibrium is the state of maximum entropy.

Entropy 2

- The direction of thermal energy transfer is not determined by energy conservation but by the change in entropy of a system.
- The change in entropy of a system, ΔS, during a process that takes the system from an initial state to a final state is defined as:

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{dQ}{T}$$

- The SI units for the change in entropy are joules per kelvin (J/K).
- This equation applies only to reversible processes.
- The integration can only be carried out over a path representing a reversible process.

Entropy 3

- Entropy is defined in terms of its change from an initial to a final configuration.
- Entropy change is the physically meaningful quantity, not the absolute value of the entropy at any point.
- Another physical quantity for which only the change is important is the potential energy.
- In a manner like the way connections between forces and potential energy changes are established, we will show how to calculate entropy changes for given temperature changes and amounts of heat and work in different systems.
- At thermal equilibrium, the entropy has an extremum (a maximum).
- At stable equilibrium, the net force is zero, and therefore the potential energy has an extremum (a minimum, in this case).

Entropy 4

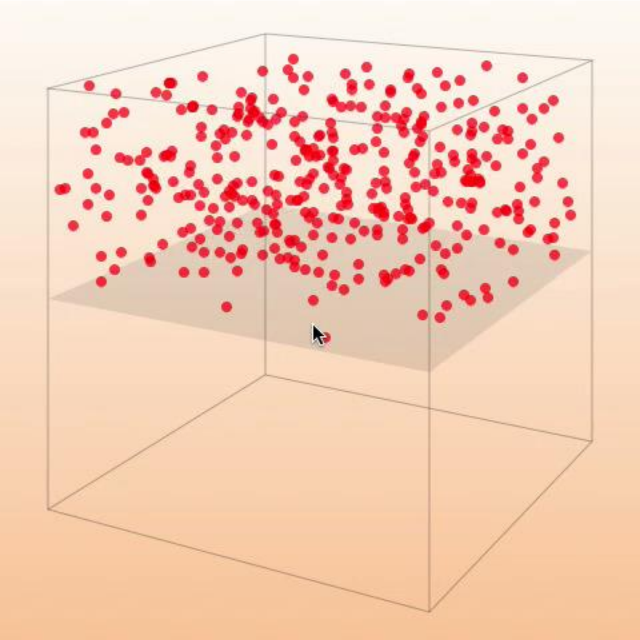
- In an irreversible process in an isolated system, the entropy, *S*, of the system never decreases; it always increases or stays constant.
- In an isolated system, energy is always conserved, but entropy is not conserved.
- Thus, the change in entropy defines a direction for time; that is, time moves forward if the entropy of an isolated system is increasing.
- The definition of entropy so far rests on the macroscopic properties of a system, such as heat and temperature.
- Another definition of entropy, based on statistical descriptions of how the atoms and molecules of a system are arranged, is presented in the next section.

Entropy 5

- Since the integral representing entropy can only be evaluated for a reversible process, how can we calculate the change in entropy for an irreversible process?
- The answer lies in the fact that entropy is a thermodynamic state variable, just like temperature, pressure, and volume.
- This means that we can calculate the entropy difference between a known initial state and a known final state even for an irreversible process, if there is a reversible process that takes the system from the same initial to the same final state.
- Perhaps this is the subtlest point about thermodynamics conveyed in this entire chapter.

Entropy 6

- To illustrate this general method of computing the change in entropy for an irreversible process, let's return to the free expansion of a gas.
- A gas is confined to the top half of a box and after some time the barrier between the two halves is removed.



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Entropy 7

- Clearly, once the gas has expanded to fill the entire volume of the box, the system will never spontaneously return to the state where all the gas molecules are in the top half of the box.
- The state variables of the system before the barrier is removed are the initial temperature, T_i, the initial volume, V_i , and the initial entropy, S_i.
- After the barrier has been removed and the gas is again in equilibrium, the state of the system can be described in terms of the final temperature, T_f , the final volume, V_f , and the final entropy, S_f.

Entropy 8

- We cannot calculate the change in entropy of this system using our integral because the gas is not in equilibrium during the expansion phase.
- However, the change in the properties of the system depends only on the initial and final states, not on how the system got from one to the other.
- Therefore, we can choose a process that the system could have undergone for which we can evaluate our integral.
- In the free expansion of an ideal gas, the temperature remains constant.
- It seems reasonable to use the isothermal expansion of an ideal gas.

Entropy 9

- We can then evaluate our integral to calculate the change in entropy of the system undergoing an isothermal process:

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{dQ}{T} = \frac{1}{T}\int_{\mathrm{i}}^{\mathrm{f}} dQ = \frac{Q}{T}$$

- The work done by an ideal gas in expanding from V_{i} to V_{f} at a constant temperature T is given by:

$$Q = nRT \ln\left(\frac{V_{\mathrm{f}}}{V_{\mathrm{i}}}\right)$$

- For an isothermal process, the internal energy of the gas does not change, so:

$$\Delta E_{\mathrm{int}} = 0$$

Entropy 10

- We can use the First Law of Thermodynamics to write:

$$\Delta E_{\text{int}} = W - Q = 0$$

- Consequently, for the isothermal process, the heat added to the system is:

$$Q = W = nRT \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)$$

- The resulting entropy change for the isothermal process is:

$$\Delta S = \frac{Q}{T} = \frac{nRT \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)}{T} = nR \ln\left(\frac{V_{\text{f}}}{V_{\text{i}}}\right)$$

Entropy 11

- The entropy change for the irreversible free expansion of a gas must be equal to the entropy change for the isothermal process because both processes have the same initial and final states and thus must have the same change in entropy.
- For the irreversible free expansion of a gas, $V_f > V_i$, and so $\ln(V_f / V_i) > 0$.
- Thus, $\Delta S > 0$ because n and R are positive numbers.
- The change in entropy of any irreversible process is always positive.
- The Second Law of Thermodynamics can be stated in a third way.

The entropy of an isolated system can never decrease.

Entropy Change for the Freezing of Water 1

- Suppose we have 1.50 kg of water at a temperature of 0 °C.
- We put the water in a freezer, and enough heat is removed from the water to freeze it completely to ice at a temperature of 0 °C.

PROBLEM:

- How much does the entropy of the water-ice system change during the freezing process?

SOLUTION:

- The melting of ice is an isothermal process, so the change in entropy is:

$$\Delta S = \frac{Q}{T}$$

Entropy Change for the Freezing of Water 2

- Q is the heat that must be removed to change the water to ice at T = 273.15 K.
- The heat that must be removed to freeze the water is determined by the latent heat of fusion of water (ice).
- The heat that must be removed is:

$$Q = mL_{\text{fusion}} = (1.50\text{ kg})(334\text{ kJ/kg}) = 501\text{ J}$$

- The change in entropy of the water-ice system is:

$$\Delta S = \frac{-501\text{ kJ}}{273.15\text{ K}} = -1830\text{ J/K}$$

Entropy Change for the Freezing of Water 3

- Note that the entropy of the water-ice system decreased.
- How can the entropy of this system decrease?
- The Second Law of Thermodynamics states that the entropy of an isolated system can never decrease.
- However, the water-ice system is not an isolated system.
- The freezer used energy to remove heat from the water to freeze it and exhausted the heat into the local environment.
- Thus, the entropy of that environment increased more than the entropy of the water-ice system decreased.
- This is a very important distinction.

Entropy

- A similar analysis can be applied to the origins of complex life forms, which have much lower entropy than their surroundings.
- The development of life forms with low entropy is accompanied by an increase in the overall entropy of the Earth.
- In order for a living subsystem of Earth to reduce its own entropy at the expense of its environment, it needs a source of energy.
- This source of energy can be chemical bonds or other types of potential energy, which in the end arises from the energy provided to Earth by solar radiation.

Entropy Change for the Warming of Water 1

- We start with 2.00 kg of water at 20.0 °C and warm the water until it reaches a temperature of 80.0 °C.

PROBLEM:

- What is the change in entropy of the water?

SOLUTION:

- We start with:

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{dQ}{T}$$

- The heat required to raise the temperature of a mass, *m*, of water is:

$$Q = cm\Delta T$$

Entropy Change for the Warming of Water 2

- We can rewrite this equation in terms of the differential change in heat, dQ, and the differential change in temperature, dT:

$$dQ = cmdT$$

- Then we can rewrite our integral as:

$$\Delta S = \int_{\mathrm{i}}^{\mathrm{f}} \frac{dQ}{T} = \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \frac{cmdT}{T} = cm \int_{T_{\mathrm{i}}}^{T_{\mathrm{f}}} \frac{dT}{T} = cm \ln \frac{T_{\mathrm{f}}}{T_{\mathrm{i}}}$$

- Putting in our numerical values gives us:

$$\Delta S = (4.19 \text{ kJ})(2.00 \text{ kg}) \ln \frac{353.15 \text{ K}}{293.15 \text{ K}} = 1.56 \cdot 10^{3} \text{ J/K}$$

Microscopic Interpretation of Entropy 1

- In Chapter 19, we saw that the internal energy of an ideal gas could be calculated by summing up the energies of the constituent particles of the gas.
- We can also determine the entropy of an ideal gas by studying the constituent particles.
- It turns out that this microscopic definition of entropy agrees with the macroscopic definition.
- The ideas of order and disorder are intuitive.
- For example, a coffee cup is an ordered system.
- Smashing the cup by dropping it on the floor creates a system that is less ordered, or more disordered, than the original system.

Microscopic Interpretation of Entropy 2

- The disorder of a system can be described quantitatively using the concept of **microscopic states**.
- Another term for a microscopic state is a *degree of freedom*.
- Suppose we toss *n* coins in the air, and half of them land heads up and half of them land tails up.
- The statement "half the coins are heads, and half the coins are tails" is a description of the macroscopic state of *n* coins.
- Each coin can have one of two microscopic states: heads or tails.
- Stating that half the coins are heads, and half the coins are tails does not specify anything about the microscopic state of each coin.

Concept Check 9

- When a coin is tossed, it can land heads up or tails up.
- You toss a coin 10 times, and it comes up heads every time.
- What is the probability that the coin will come up heads on the 11th toss?

A. 10%

B. 20%

C. 50%

D. 90%

E. 100%

Solution Concept Check 9

- When a coin is tossed, it can land heads up or tails up.
- You toss a coin 10 times, and it comes up heads every time.
- What is the probability that the coin will come up heads on the 11th toss?

A. 10%

B. 20%

[✓ C. 50%]

D. 90%

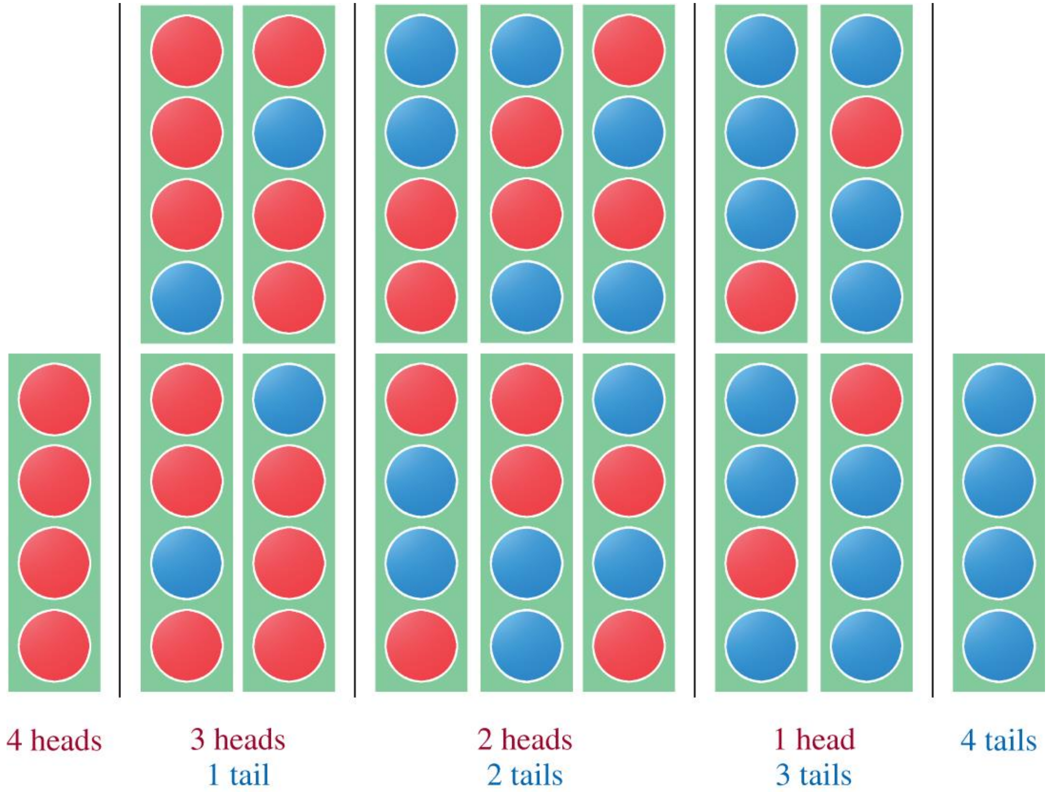
E. 100%

Microscopic Interpretation of Entropy 3

- However, if all the coins are heads or all the coins are tails, the microscopic state of each coin is known.
- The macroscopic state consisting of half heads and half tails is a disordered system because very little is known about the microscopic state of each coin.
- The macroscopic state with all heads or the macroscopic state with all tails is an ordered system because the microscopic state of each coin is known.
- To quantify this concept, imagine tossing four coins in the air.
- There is only one way to get four heads, four ways to get three heads and one tail, six ways to get two heads and two tails, four ways to get one head and three tails, and only one way to get four tails.

Microscopic Interpretation of Entropy 4

- There are five possible macroscopic states and sixteen possible microscopic states.



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Concept Check 10

- The number of macrostates that can result from rolling a set of N six-sided dice is the number of different totals that can be obtained by adding the pips on the N faces that end up on top.
- The number of macrostates is

A. 6^N.

B. $6N$.

C. $6N - 1$.

D. $5N + 1$.

Solution Concept Check 10

- The number of macrostates that can result from rolling a set of N six-sided dice is the number of different totals that can be obtained by adding the pips on the N faces that end up on top.
- The number of macrostates is

A. 6^N.
B. $6N$.
C. $6N - 1$.
D. $5N + 1$.

2 dice: can add to 2 through 12 ⇒ 11 macrostates
3 dice: can add to 3 through 18 ⇒ 16 macrostates
4 dice: can add to 4 through 24 ⇒ 21 macrostates
5 dice: can add to 5 through 30 ⇒ 26 macrostates
$\Rightarrow 5N + 1$

Microscopic Interpretation of Entropy 5

- Suppose we toss fifty coins in the air instead of four coins.
- There are $2^{50} = 1.13 \cdot 10^{15}$ possible microstates of this system of fifty tossed coins.
- The most probable macroscopic state consists of half heads and half tails.
- There are $1.26 \cdot 10^{14}$ possible microstates with half heads and half tails.
- The probability that half the coins will be heads and half will be tails is 11.2%, while the probability of having all fifty coins land heads up is 1 in $1.13 \cdot 10^{15}$.

Microscopic Interpretation of Entropy 6

- Let's apply these concepts to a real system of gas molecules: a mole of gas, or Avogadro's number of molecules, at pressure p, volume V, and temperature T.
- These three quantities describe the macroscopic state of the gas.
- The microscopic description of the system needs to specify the momentum and position of each molecule of the gas.
- Each molecule has three components of its momentum and three components of its position.
- At any given time, the gas can be in an extremely large number of microscopic states, depending on the positions and velocities of each of its $6.02 \cdot 10^{23}$ molecules.

Microscopic Interpretation of Entropy 7

- If the gas undergoes free expansion, the number of possible microscopic states increases, and the system becomes more disordered.
- Because the entropy of a gas undergoing free expansion increases, the increase in disorder is related to the increase of entropy.
- This idea can be generalized as follows:

The most probable macroscopic state of a system is the state with the largest number of microscopic states, which is also the macroscopic state with the greatest disorder.

Microscopic Interpretation of Entropy 8

- Let w be the number of possible microscopic states for a given macroscopic state.
- It can be shown that the entropy of the macroscopic state is given by:

  $$S = k_{\mathrm{B}} \ln w$$

- This equation was first written down by the Austrian physicist Ludwig Boltzmann and is his most significant accomplishment (it is chiseled into his tombstone).
- You can see that increasing the number of possible microscopic states increases the entropy.
- The important aspect of a thermodynamic process is not the absolute entropy, but the change in entropy between an initial state and a final state.

Microscopic Interpretation of Entropy 9

- Taking this definition of entropy, the smallest number of microstates is one and the smallest entropy that can exist is then zero.
- According to this definition, entropy can never be negative.
- In practice, determining the number of possible microscopic states is difficult except for special systems.
- However, the change in the number of possible microscopic states can often be determined, thus allowing the change in entropy of the system to be found.
- Consider a system that initially has w_i microstates and then undergoes a thermodynamic process to a macroscopic state with w_f microstates.

Microscopic Interpretation of Entropy 10

- The change in entropy is:

$$\Delta S = S_{\text{f}} - S_{\text{i}} = k_{\text{B}} \ln w_{\text{f}} - k_{\text{B}} \ln w_{\text{i}} = k_{\text{B}} \ln \frac{w_{\text{f}}}{w_{\text{i}}}$$

- Thus, the change in entropy between two macroscopic states depends on the ratio of the number of possible microstates.
- The definition of the entropy of a system in terms of the number of possible microstates leads to further insight into the Second Law of Thermodynamics, which states that the entropy of an isolated system can never decrease.
- This means that an isolated system can never undergo a thermodynamic process that lowers the number of possible microstates.

Microscopic Interpretation of Entropy 11

- For example, if our free expansion of a gas were to occur in reverse—that is, the gas underwent free contraction into a volume half its original size—the number of possible microstates for each molecule would decrease a factor of 2.
- The probability of finding one gas molecule in half of the original volume then is $1/2$, and the probability of finding all the gas molecules in half of the original volume is $(1/2)^N$, where N is the number of molecules.
- If there are 100 gas molecules in the system, the probability that all 100 molecules end up in half the original volume is $7.9 \cdot 10^{-31}$.
- We would have to check the system approximately $1/(7.9 \cdot 10^{-31}) \approx 10^{30}$ times to find the molecules in half the volume just once.

Microscopic Interpretation of Entropy 12

- Checking once per second, this would take about 10^{13} billion years, whereas the age of the universe is only 13.7 billion years.
- If the system contains Avogadro's number of gas molecules, then the probability that the molecules will all be in half of the volume is even smaller.
- Thus, although the probability that this process will happen is not zero, it is so small that we can treat it as zero.
- We can thus conclude that the Second Law of Thermodynamics, even if expressed in terms of probabilities, is never violated in any practical situation.

Entropy Increase during Free Expansion of a Gas 1

- Initially 0.500 mole of nitrogen gas is confined to a volume of 0.500 m^3.
- When the barrier is removed, the gas expands to fill the new volume of 1.00 m^3.

PROBLEM:

- What is the change in entropy of the gas?

SOLUTION:

- Assuming we can treat the system as an isothermal expansion of an ideal gas, the change in entropy is:

$$\Delta S = nR \ln\left(\frac{V_\text{f}}{V_\text{i}}\right) = nR \ln\left(\frac{1.00\ \text{m}^3}{0.500\ \text{m}^3}\right) = nR \ln 2$$

$$\Delta S = (0.500\ \text{mol})\big(8.31\ \text{J}/(\text{mol K})\big)(\ln 2) = 2.88\ \text{J/K}$$

Entropy Increase during Free Expansion of a Gas 2

- Another approach is to examine the number of microstates of the system before and after the expansion to calculate the change in entropy.
- In this system, the number of gas molecules is:

$N = nN_{\mathrm{A}}$

- Before the expansion, there were w_{i} microstates for the gas molecules in the left half of the container.
- After the expansion, any of the molecules could be in the left half or the right half of the container.
- Therefore, the number of microstates after the expansion is:

$w_{\mathrm{f}} = 2^{N} w_{\mathrm{i}}$

Entropy Increase during Free Expansion of a Gas 3

- Remembering that $nR = Nk_\text{B}$, we can express the change in entropy of the system as:

$$\Delta S = k_\text{B} \ln\left(\frac{w_\text{f}}{w_\text{i}}\right) = k_\text{B} \ln\left(\frac{2^N w_\text{i}}{w_\text{i}}\right) = Nk_\text{B} \ln 2 = nR \ln 2$$

- Thus, we get the same result for the change in entropy of a freely expanding gas by looking at the microscopic properties of the system as by using the macroscopic properties of the system.

Concept Check 11

- All reversible thermodynamic processes always proceed at
  - A. constant pressure.
  - B. constant temperature.
  - C. constant entropy.
  - D. constant volume.
  - E. none of the above.

Solution Concept Check 11

- All reversible thermodynamic processes always proceed at

  A. constant pressure.

  B. constant temperature.

  C. constant entropy.

  D. constant volume.

  [✓ E. none of the above.]

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