4 | THE SECOND LAW OF THERMODYNAMICS

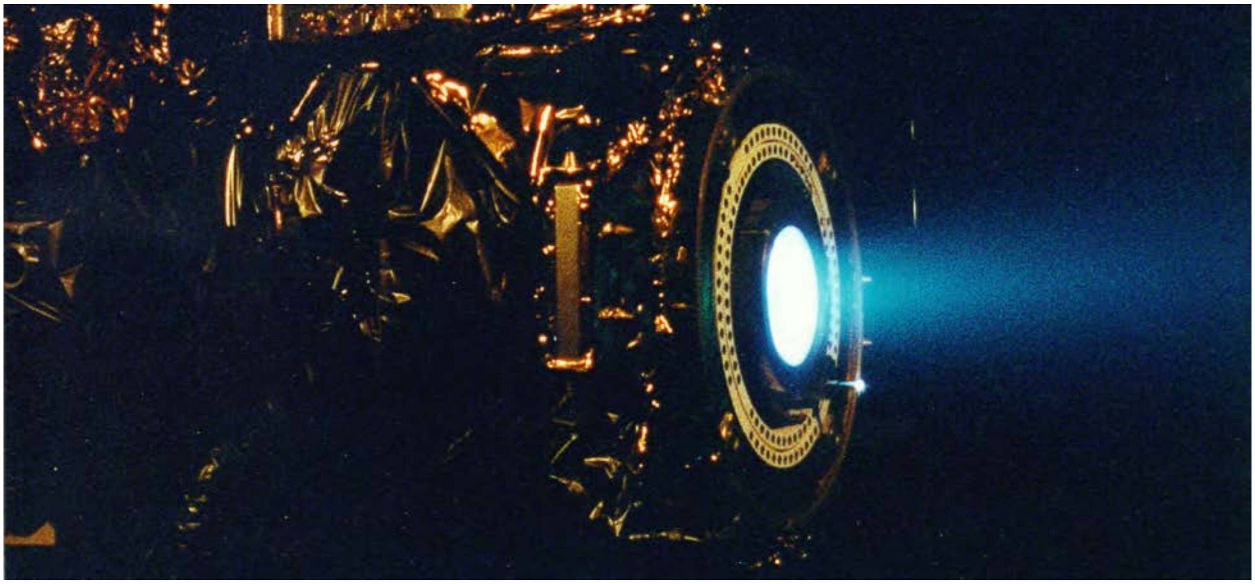


Figure 4.1 A xenon ion engine from the Jet Propulsion Laboratory shows the faint blue glow of charged atoms emitted from the engine. The ion propulsion engine is the first nonchemical propulsion to be used as the primary means of propelling a spacecraft.

Chapter Outline

Introduction

According to the first law of thermodynamics, the only processes that can occur are those that conserve energy. But this cannot be the only restriction imposed by nature, because many seemingly possible thermodynamic processes that would conserve energy do not occur. For example, when two bodies are in thermal contact, heat never flows from the colder body to the warmer one, even though this is not forbidden by the first law. So some other thermodynamic principles must be controlling the behavior of physical systems.

One such principle is the *second law of thermodynamics*, which limits the use of energy within a source. Energy cannot arbitrarily pass from one object to another, just as we cannot transfer heat from a cold object to a hot one without doing any work. We cannot unmix cream from coffee without a chemical process that changes the physical characteristics of the system or its environment. We cannot use internal energy stored in the air to propel a car, or use the energy of the ocean to run a ship, without disturbing something around that object.

In the chapter covering the first law of thermodynamics, we started our discussion with a joke by C. P. Snow stating that the first law means “you can’t win.” He paraphrased the second law as “you can’t break even, except on a very cold day.” Unless you are at zero kelvin, you cannot convert 100% of thermal energy into work. We start by discussing spontaneous processes and explain why some processes require work to occur even if energy would have been conserved.

4.1 | Reversible and Irreversible Processes

Learning Objectives

By the end of this section, you will be able to:

- Define reversible and irreversible processes
- State the second law of thermodynamics via an irreversible process

Consider an ideal gas that is held in half of a thermally insulated container by a wall in the middle of the container. The other half of the container is under vacuum with no molecules inside. Now, if we remove the wall in the middle quickly, the gas expands and fills up the entire container immediately, as shown in **Figure 4.2**.

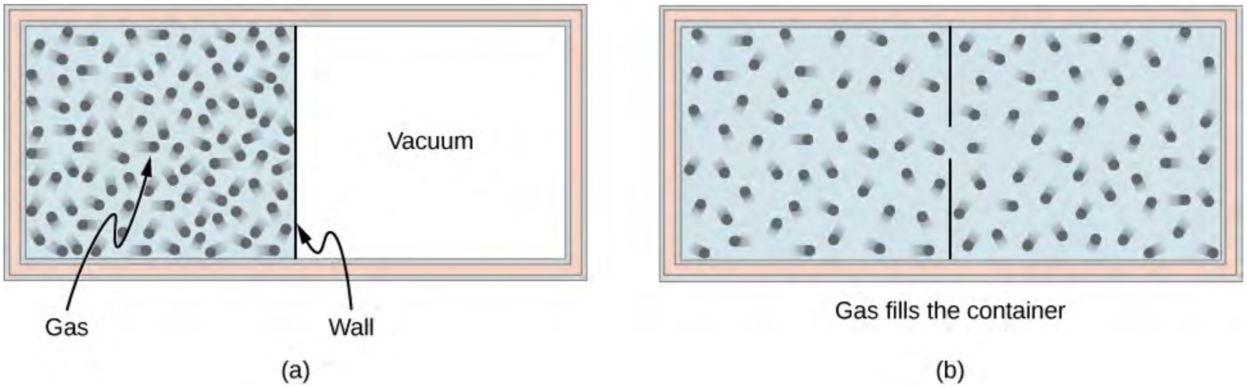


Figure 4.2 A gas expanding from half of a container to the entire container (a) before and (b) after the wall in the middle is removed.

Because half of the container is under vacuum before the gas expands there, we do not expect any work to be done by the system—that is, $W = 0$—because no force from the vacuum is exerted on the gas during the expansion. If the container is thermally insulated from the rest of the environment, we do not expect any heat transfer to the system either, so $Q = 0$. Then the first law of thermodynamics leads to the change of the internal energy of the system,

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

For an ideal gas, if the internal energy doesn’t change, then the temperature stays the same. Thus, the equation of state of the ideal gas gives us the final pressure of the gas, $p = nRT/V = p_0/2,$ where p_0 is the pressure of the gas before the expansion. The volume is doubled and the pressure is halved, but nothing else seems to have changed during the expansion.

All of this discussion is based on what we have learned so far and makes sense. Here is what puzzles us: Can all the molecules go backward to the original half of the container in some future time? Our intuition tells us that this is going to be very unlikely, even though nothing we have learned so far prevents such an event from happening, regardless of how small the probability is. What we are really asking is whether the expansion into the vacuum half of the container is *reversible*.

A **reversible process** is a process in which the system and environment can be restored to exactly the same initial states that they were in before the process occurred, if we go backward along the path of the process. The necessary condition for a reversible process is therefore the quasi-static requirement. Note that it is quite easy to restore a system to its original state; the hard part is to have its environment restored to its original state at the same time. For example, in the example of an ideal gas expanding into vacuum to twice its original volume, we can easily push it back with a piston and restore its temperature and pressure by removing some heat from the gas. The problem is that we cannot do it without changing something in its surroundings, such as dumping some heat there.

A reversible process is truly an ideal process that rarely happens. We can make certain processes close to reversible and therefore use the consequences of the corresponding reversible processes as a starting point or reference. In reality, almost all processes are irreversible, and some properties of the environment are altered when the properties of the system are restored. The expansion of an ideal gas, as we have just outlined, is irreversible because the process is not even quasi-static, that is, not in an equilibrium state at any moment of the expansion.

From the microscopic point of view, a particle described by Newton's second law can go backward if we flip the direction of time. But this is not the case, in practical terms, in a macroscopic system with more than 10^{23} particles or molecules, where numerous collisions between these molecules tend to erase any trace of memory of the initial trajectory of each of the particles. For example, we can actually estimate the chance for all the particles in the expanded gas to go back to the original half of the container, but the current age of the universe is still not long enough for it to happen even once.

An **irreversible process** is what we encounter in reality almost all the time. The system and its environment cannot be restored to their original states at the same time. Because this is what happens in nature, it is also called a natural process. The sign of an irreversible process comes from the finite gradient between the states occurring in the actual process. For example, when heat flows from one object to another, there is a finite temperature difference (gradient) between the two objects. More importantly, at any given moment of the process, the system most likely is not at equilibrium or in a well-defined state. This phenomenon is called **irreversibility**.

Let us see another example of irreversibility in thermal processes. Consider two objects in thermal contact: one at temperature T_1 and the other at temperature $T_2 > T_1$, as shown in **Figure 4.3**.

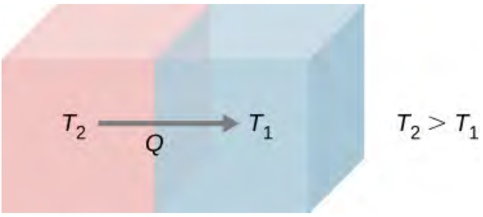


Figure 4.3 Spontaneous heat flow from an object at higher temperature T_2 to another at lower temperature T_1.

We know from common personal experience that heat flows from a hotter object to a colder one. For example, when we hold a few pieces of ice in our hands, we feel cold because heat has left our hands into the ice. The opposite is true when we hold one end of a metal rod while keeping the other end over a fire. Based on all of the experiments that have been done on spontaneous heat transfer, the following statement summarizes the governing principle:

Second Law of Thermodynamics (Clausius statement)

Heat never flows spontaneously from a colder object to a hotter object.

This statement turns out to be one of several different ways of stating the second law of thermodynamics. The form of this statement is credited to German physicist Rudolf Clausius (1822−1888) and is referred to as the **Clausius statement of the second law of thermodynamics**. The word "spontaneously" here means no other effort has been made by a third party, or one that is neither the hotter nor colder object. We will introduce some other major statements of the second law and show that they imply each other. In fact, all the different statements of the second law of thermodynamics can be shown to be equivalent, and all lead to the irreversibility of spontaneous heat flow between macroscopic objects of a very large number of molecules or particles.

Both isothermal and adiabatic processes sketched on a pV graph (discussed in **The First Law of Thermodynamics**) are reversible in principle because the system is always at an equilibrium state at any point of the processes and can go forward or backward along the given curves. Other idealized processes can be represented by pV curves; **Table 4.1** summarizes the most common reversible processes.

Process	Constant Quantity and Resulting Fact
Isobaric	Constant pressure $W = p\Delta V$
Isochoric	Constant volume $W = 0$

Table 4.1 Summary of Simple Thermodynamic Processes

Process	Constant Quantity and Resulting Fact
Isothermal	Constant temperature $\Delta T = 0$
Adiabatic	No heat transfer $Q = 0$

Table 4.1 Summary of Simple Thermodynamic Processes

4.2 | Heat Engines

Learning Objectives

By the end of this section, you will be able to:

- Describe the function and components of a heat engine
- Explain the efficiency of an engine
- Calculate the efficiency of an engine for a given cycle of an ideal gas

A **heat engine** is a device used to extract heat from a source and then convert it into mechanical work that is used for all sorts of applications. For example, a steam engine on an old-style train can produce the work needed for driving the train. Several questions emerge from the construction and application of heat engines. For example, what is the maximum percentage of the heat extracted that can be used to do work? This turns out to be a question that can only be answered through the second law of thermodynamics.

The second law of thermodynamics can be formally stated in several ways. One statement presented so far is about the direction of spontaneous heat flow, known as the Clausius statement. A couple of other statements are based on heat engines. *Whenever we consider heat engines and associated devices such as refrigerators and heat pumps, we do not use the normal sign convention for heat and work*. For convenience, we assume that the symbols $Q_\text{h}, Q_\text{c},$ and W represent only the amounts of heat transferred and work delivered, regardless what the givers or receivers are. Whether heat is entering or leaving a system and work is done to or by a system are indicated by proper signs in front of the symbols and by the directions of arrows in diagrams.

It turns out that we need more than one heat source/sink to construct a heat engine. We will come back to this point later in the chapter, when we compare different statements of the second law of thermodynamics. For the moment, we assume that a heat engine is constructed between a heat source (high-temperature reservoir or hot reservoir) and a heat sink (low-temperature reservoir or cold reservoir), represented schematically in Figure 4.4. The engine absorbs heat Q_h from a heat source (**hot reservoir**) of Kelvin temperature $T_\text{h},$ uses some of that energy to produce useful work W, and then discards the remaining energy as heat Q_c into a heat sink (**cold reservoir**) of Kelvin temperature $T_\text{c}.$ Power plants and internal combustion engines are examples of heat engines. Power plants use steam produced at high temperature to drive electric generators, while exhausting heat to the atmosphere or a nearby body of water in the role of the heat sink. In an internal combustion engine, a hot gas-air mixture is used to push a piston, and heat is exhausted to the nearby atmosphere in a similar manner.

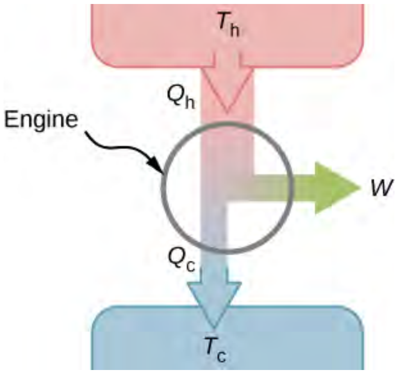


Figure 4.4 A schematic representation of a heat engine. Energy flows from the hot reservoir to the cold reservoir while doing work.

Actual heat engines have many different designs. Examples include internal combustion engines, such as those used in most cars today, and external combustion engines, such as the steam engines used in old steam-engine trains. **Figure 4.5** shows a photo of a nuclear power plant in operation. The atmosphere around the reactors acts as the cold reservoir, and the heat generated from the nuclear reaction provides the heat from the hot reservoir.

Figure 4.5 The heat exhausted from a nuclear power plant goes to the cooling towers, where it is released into the atmosphere.

Heat engines operate by carrying a *working substance* through a cycle. In a steam power plant, the working substance is water, which starts as a liquid, becomes vaporized, is then used to drive a turbine, and is finally condensed back into the liquid state. As is the case for all working substances in cyclic processes, once the water returns to its initial state, it repeats the same sequence.

For now, we assume that the cycles of heat engines are reversible, so there is no energy loss to friction or other irreversible effects. Suppose that the engine of **Figure 4.4** goes through one complete cycle and that Q_h, Q_c, and W represent the heats exchanged and the work done for that cycle. Since the initial and final states of the system are the same, $\Delta E_{int} = 0$ for the cycle. We therefore have from the first law of thermodynamics,

$$W = Q - \Delta E_{int} = (Q_h - Q_c) - 0,$$

so that

$$W = Q_h - Q_c. \tag{4.1}$$

The most important measure of a heat engine is its **efficiency (*e*)**, which is simply "what we get out" divided by "what we put in" during each cycle, as defined by $e = W_{out}/Q_{in}$.

With a heat engine working between two heat reservoirs, we get out W and put in Q_h, so the efficiency of the engine is

$$e = \frac{W}{Q_\text{h}} = 1 - \frac{Q_\text{c}}{Q_\text{h}}. \tag{4.2}$$

Here, we used **Equation 4.1**, $W = Q_\text{h} - Q_\text{c}$, in the final step of this expression for the efficiency.

Example 4.1

A Lawn Mower

A lawn mower is rated to have an efficiency of 25.0% and an average power of 3.00 kW. What are (a) the average work and (b) the minimum heat discharge into the air by the lawn mower in one minute of use?

Strategy

From the average power—that is, the rate of work production—we can figure out the work done in the given elapsed time. Then, from the efficiency given, we can figure out the minimum heat discharge $Q_\text{c} = Q_\text{h}(1 - e)$ with $Q_\text{h} = Q_\text{c} + W$.

Solution

a. The average work delivered by the lawn mower is

$$W = P\Delta t = 3.00 \times 10^3 \times 60 \times 1.00\,\text{J} = 180\,\text{kJ}.$$

b. The minimum heat discharged into the air is given by

$$Q_\text{c} = Q_\text{h}(1 - e) = (Q_\text{c} + W)(1 - e),$$

which leads to

$$Q_\text{c} = W(1/e - 1) = 180 \times (1/0.25 - 1)\,\text{kJ} = 540\,\text{kJ}.$$

Significance

As the efficiency rises, the minimum heat discharged falls. This helps our environment and atmosphere by not having as much waste heat expelled.

4.3 | Refrigerators and Heat Pumps

Learning Objectives

By the end of this section, you will be able to:

- Describe a refrigerator and a heat pump and list their differences
- Calculate the performance coefficients of simple refrigerators and heat pumps

The cycles we used to describe the engine in the preceding section are all reversible, so each sequence of steps can just as easily be performed in the opposite direction. In this case, the engine is known as a refrigerator or a heat pump, depending on what is the focus: the heat removed from the cold reservoir or the heat dumped to the hot reservoir. Either a refrigerator or a heat pump is an engine running in reverse. For a **refrigerator**, the focus is on removing heat from a specific area. For a **heat pump**, the focus is on dumping heat to a specific area.

We first consider a refrigerator (**Figure 4.6**). The purpose of this engine is to remove heat from the cold reservoir, which is the space inside the refrigerator for an actual household refrigerator or the space inside a building for an air-conditioning unit.

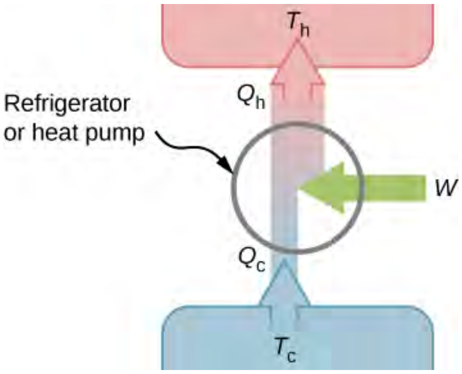


Figure 4.6 A schematic representation of a refrigerator (or a heat pump). The arrow next to work (W) indicates work being put into the system.

A refrigerator (or heat pump) absorbs heat Q_c from the cold reservoir at Kelvin temperature T_c and discards heat Q_h to the hot reservoir at Kelvin temperature $T_h,$ while work W is done on the engine's working substance, as shown by the arrow pointing toward the system in the figure. A household refrigerator removes heat from the food within it while exhausting heat to the surrounding air. The required work, for which we pay in our electricity bill, is performed by the motor that moves a coolant through the coils. A schematic sketch of a household refrigerator is given in **Figure 4.7**.

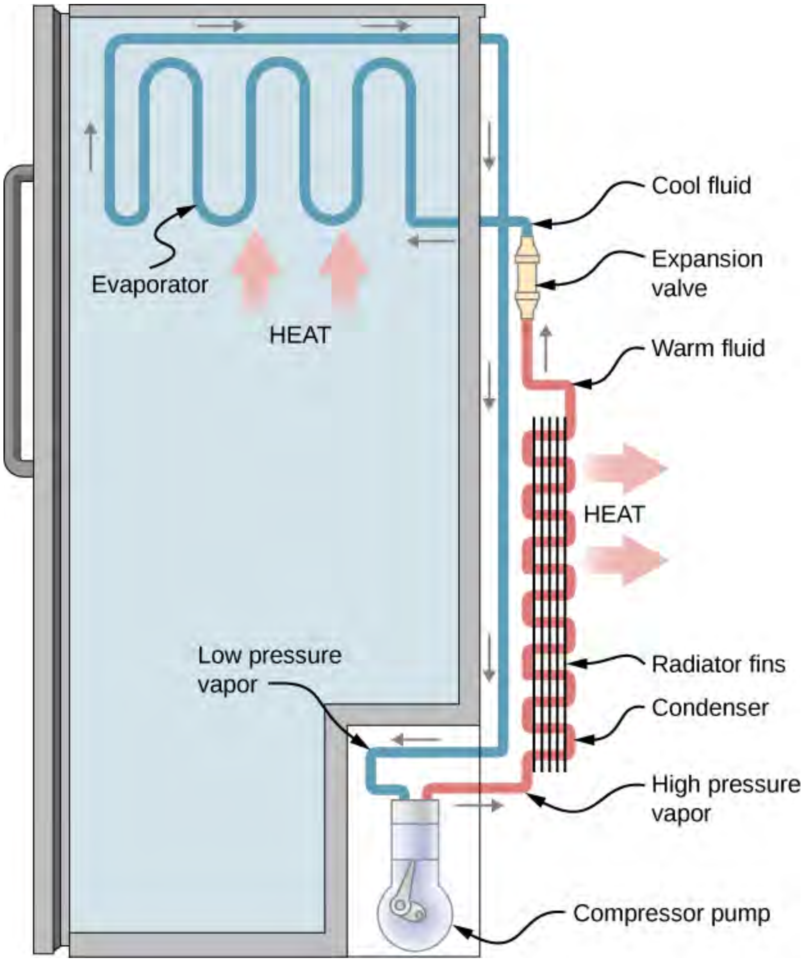


Figure 4.7 A schematic diagram of a household refrigerator. A coolant with a boiling temperature below the freezing point of water is sent through the cycle (clockwise in this diagram). The coolant extracts heat from the refrigerator at the evaporator, causing coolant to vaporize. It is then compressed and sent through the condenser, where it exhausts heat to the outside.

The effectiveness or **coefficient of performance** K_R of a refrigerator is measured by the heat removed from the cold reservoir divided by the work done by the working substance cycle by cycle:

$$K_R = \frac{Q_c}{W} = \frac{Q_c}{Q_h - Q_c}. \tag{4.3}$$

Note that we have used the condition of energy conservation, $W = Q_h - Q_c$, in the final step of this expression.

The effectiveness or coefficient of performance K_P of a heat pump is measured by the heat dumped to the hot reservoir divided by the work done to the engine on the working substance cycle by cycle:

$$K_P = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}. \tag{4.4}$$

Once again, we use the energy conservation condition $W = Q_h - Q_c$ to obtain the final step of this expression.

4.4 | Statements of the Second Law of Thermodynamics

Learning Objectives

By the end of this section, you will be able to:

- Contrast the second law of thermodynamics statements according to Kelvin and Clausius formulations
- Interpret the second of thermodynamics via irreversibility

Earlier in this chapter, we introduced the Clausius statement of the second law of thermodynamics, which is based on the irreversibility of spontaneous heat flow. As we remarked then, the second law of thermodynamics can be stated in several different ways, and all of them can be shown to imply the others. In terms of heat engines, the second law of thermodynamics may be stated as follows:

Second Law of Thermodynamics (Kelvin statement)

It is impossible to convert the heat from a single source into work without any other effect.

This is known as the **Kelvin statement of the second law of thermodynamics**. This statement describes an unattainable “ **perfect engine**,” as represented schematically in Figure 4.8(a). Note that “without any other effect” is a very strong restriction. For example, an engine can absorb heat and turn it all into work, *but not if it completes a cycle*. Without completing a cycle, the substance in the engine is not in its original state and therefore an “other effect” has occurred. Another example is a chamber of gas that can absorb heat from a heat reservoir and do work isothermally against a piston as it expands. However, if the gas were returned to its initial state (that is, made to complete a cycle), it would have to be compressed and heat would have to be extracted from it.

The Kelvin statement is a manifestation of a well-known engineering problem. Despite advancing technology, we are not able to build a heat engine that is 100% efficient. The first law does not exclude the possibility of constructing a perfect engine, but the second law forbids it.

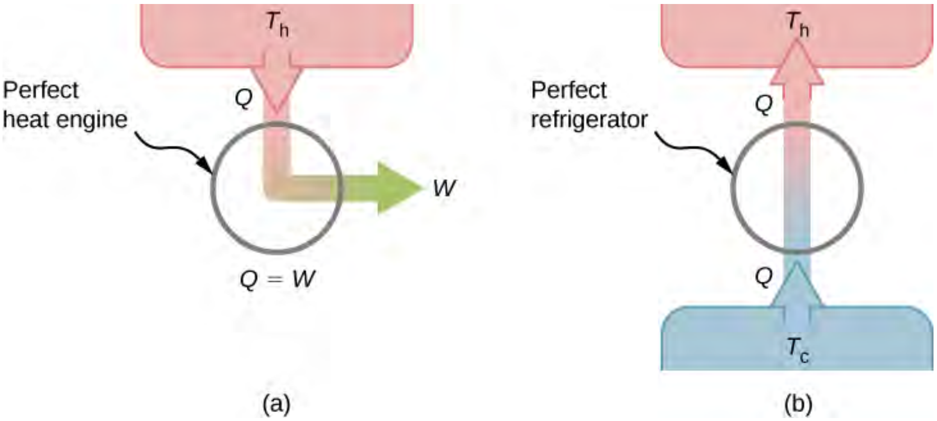


Figure 4.8 (a) A “perfect heat engine” converts all input heat into work. (b) A “perfect refrigerator” transports heat from a cold reservoir to a hot reservoir without work input. Neither of these devices is achievable in reality.

We can show that the Kelvin statement is equivalent to the Clausius statement if we view the two objects in the Clausius statement as a cold reservoir and a hot reservoir. Thus, the Clausius statement becomes: *It is impossible to construct a refrigerator that transfers heat from a cold reservoir to a hot reservoir without aid from an external source*. The Clausius statement is related to the everyday observation that heat never flows spontaneously from a cold object to a hot object. *Heat transfer in the direction of increasing temperature always requires some energy input*. A “ **perfect refrigerator**,” shown in Figure 4.8(b), which works without such external aid, is impossible to construct.

To prove the equivalence of the Kelvin and Clausius statements, we show that if one statement is false, it necessarily follows that the other statement is also false. Let us first assume that the Clausius statement is false, so that the perfect refrigerator of **Figure 4.8**(b) does exist. The refrigerator removes heat Q from a cold reservoir at a temperature T_c and transfers all of it to a hot reservoir at a temperature T_h. Now consider a real heat engine working in the same temperature range. It extracts heat $Q + \Delta Q$ from the hot reservoir, does work W, and discards heat Q to the cold reservoir. From the first law, these quantities are related by $W = (Q + \Delta Q) - Q = \Delta Q$.

Suppose these two devices are combined as shown in **Figure 4.9**. The net heat removed from the hot reservoir is ΔQ, no net heat transfer occurs to or from the cold reservoir, and work W is done on some external body. Since $W = \Delta Q$, the combination of a perfect refrigerator and a real heat engine is itself a perfect heat engine, thereby contradicting the Kelvin statement. Thus, if the Clausius statement is false, the Kelvin statement must also be false.

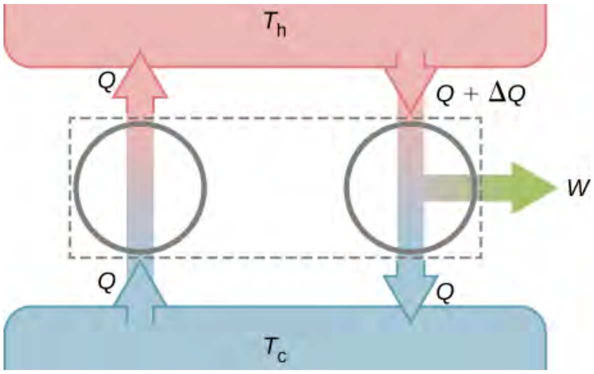


Figure 4.9 Combining a perfect refrigerator and a real heat engine yields a perfect heat engine because $W = \Delta Q$.

Using the second law of thermodynamics, we now prove two important properties of heat engines operating between two heat reservoirs. The first property is that *any reversible engine operating between two reservoirs has a greater efficiency than any irreversible engine operating between the same two reservoirs*.

The second property to be demonstrated is that *all reversible engines operating between the same two reservoirs have the same efficiency*. To show this, we start with the two engines D and E of **Figure 4.10**(a), which are operating between two common heat reservoirs at temperatures T_h and T_c. First, we assume that D is a reversible engine and that E is a hypothetical irreversible engine that has a higher efficiency than D. If both engines perform the same amount of work W per cycle, it follows from **Equation 4.2** that $Q_h > Q'_h$. It then follows from the first law that $Q_c > Q'_c$.

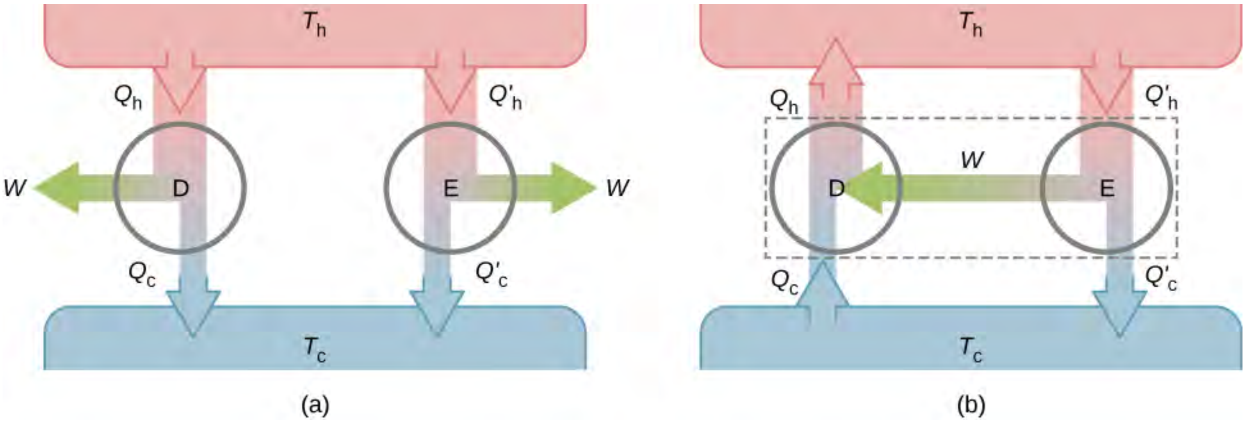


Figure 4.10 (a) Two uncoupled engines D and E working between the same reservoirs. (b) The coupled engines, with D working in reverse.

Suppose the cycle of D is reversed so that it operates as a refrigerator, and the two engines are coupled such that the work output of E is used to drive D, as shown in **Figure 4.10**(b). Since $Q_h > Q'_h$ and $Q_c > Q'_c$, the net result of each cycle is equivalent to a spontaneous transfer of heat from the cold reservoir to the hot reservoir, a process the second law does not allow. The original assumption must therefore be wrong, and it is impossible to construct an irreversible engine such that E is more efficient than the reversible engine D.

Now it is quite easy to demonstrate that the efficiencies of all reversible engines operating between the same reservoirs are equal. Suppose that D and E are both reversible engines. If they are coupled as shown in Figure 4.10(b), the efficiency of E cannot be greater than the efficiency of D, or the second law would be violated. If both engines are then reversed, the same reasoning implies that the efficiency of D cannot be greater than the efficiency of E. Combining these results leads to the conclusion that all reversible engines working between the same two reservoirs have the same efficiency.

4.1 Check Your Understanding What is the efficiency of a perfect heat engine? What is the coefficient of performance of a perfect refrigerator?

4.2 Check Your Understanding Show that $Q_\mathrm{h} - Q'_\mathrm{h} = Q_\mathrm{c} - Q'_\mathrm{c}$ for the hypothetical engine of Figure 4.10(b).

4.5 | The Carnot Cycle

Learning Objectives

- Describe the Carnot cycle with the roles of all four processes involved
- Outline the Carnot principle and its implications
- Demonstrate the equivalence of the Carnot principle and the second law of thermodynamics

In the early 1820s, Sadi Carnot (1786−1832), a French engineer, became interested in improving the efficiencies of practical heat engines. In 1824, his studies led him to propose a hypothetical working cycle with the highest possible efficiency between the same two reservoirs, known now as the **Carnot cycle**. An engine operating in this cycle is called a **Carnot engine**. The Carnot cycle is of special importance for a variety of reasons. At a practical level, this cycle represents a reversible model for the steam power plant and the refrigerator or heat pump. Yet, it is also very important theoretically, for it plays a major role in the development of another important statement of the second law of thermodynamics. Finally, because only two reservoirs are involved in its operation, it can be used along with the second law of thermodynamics to define an absolute temperature scale that is truly independent of any substance used for temperature measurement.

With an ideal gas as the working substance, the steps of the Carnot cycle, as represented by Figure 4.11, are as follows.

1. *Isothermal expansion.* The gas is placed in thermal contact with a heat reservoir at a temperature T_h. The gas absorbs heat Q_h from the heat reservoir and is allowed to expand isothermally, doing work W_1. Because the internal energy E_int of an ideal gas is a function of the temperature only, the change of the internal energy is zero, that is, $\Delta E_\mathrm{int} = 0$ during this isothermal expansion. With the first law of thermodynamics, $\Delta E_\mathrm{int} = Q - W,$ we find that the heat absorbed by the gas is

$$Q_\mathrm{h} = W_1 = nRT_\mathrm{h}\ \ln\frac{V_N}{V_M}.$$

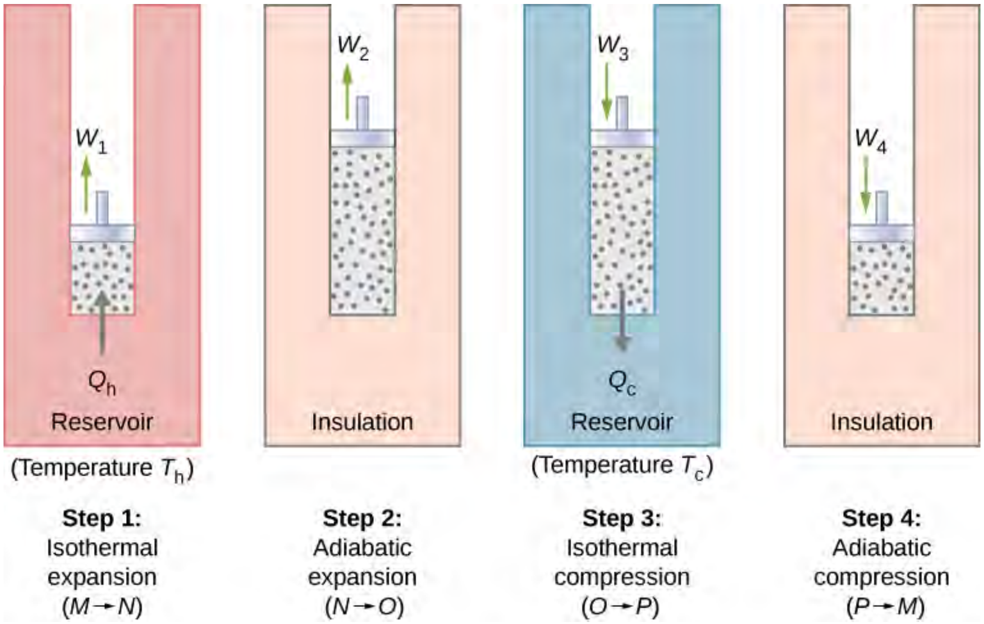


Figure 4.11 The four processes of the Carnot cycle. The working substance is assumed to be an ideal gas whose thermodynamic path *MNOP* is represented in **Figure 4.12**.

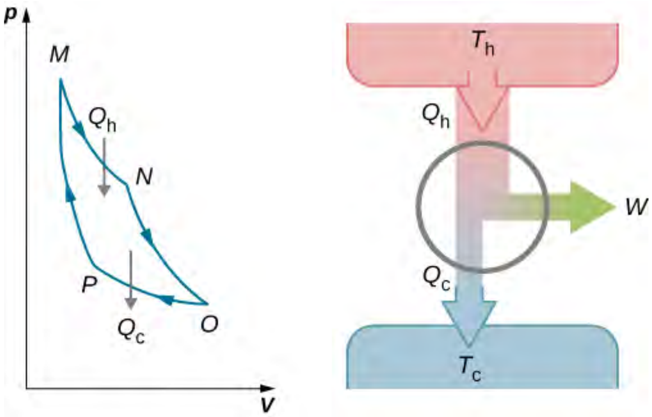


Figure 4.12 The total work done by the gas in the Carnot cycle is shown and given by the area enclosed by the loop *MNOPM*.

2. *Adiabatic expansion*. The gas is thermally isolated and allowed to expand further, doing work W_2. Because this expansion is adiabatic, the temperature of the gas falls—in this case, from T_h to T_c. From $pV^\gamma =$ constant and the equation of state for an ideal gas, $pV = nRT$, we have

$$TV^{\gamma - 1} = \text{constant},$$

so that

$$T_h V_N{}^{\gamma - 1} = T_c V_O{}^{\gamma - 1}.$$

3. *Isothermal compression*. The gas is placed in thermal contact with a cold reservoir at temperature T_c and compressed isothermally. During this process, work W_3 is done on the gas and it gives up heat Q_c to the cold reservoir. The reasoning used in step 1 now yields

$$Q_c = nRT_c \ln\frac{V_O}{V_P},$$

where Q_c is the heat dumped to the cold reservoir by the gas.

4. *Adiabatic compression*. The gas is thermally isolated and returned to its initial state by compression. In this process, work W_4 is done on the gas. Because the compression is adiabatic, the temperature of the gas rises—from T_c to T_h in this particular case. The reasoning of step 2 now gives

$$T_c V_P{}^{\gamma - 1} = T_h V_M{}^{\gamma - 1}.$$

The total work done by the gas in the Carnot cycle is given by

$$W = W_1 + W_2 - W_3 - W_4.$$

This work is equal to the area enclosed by the loop shown in the *pV* diagram of **Figure 4.12**. Because the initial and final states of the system are the same, the change of the internal energy of the gas in the cycle must be zero, that is, $\Delta E_{\text{int}} = 0$. The first law of thermodynamics then gives

$$W = Q - \Delta E_{\text{int}} = (Q_h - Q_c) - 0,$$

and

$$W = Q_h - Q_c.$$

To find the efficiency of this engine, we first divide Q_c by Q_h:

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}\frac{\ln V_O/V_P}{\ln V_N/V_M}.$$

When the adiabatic constant from step 2 is divided by that of step 4, we find

$$\frac{V_O}{V_P} = \frac{V_N}{V_M}.$$

Substituting this into the equation for Q_c/Q_h, we obtain

$$\frac{Q_c}{Q_h} = \frac{T_c}{T_h}.$$

Finally, with **Equation 4.2**, we find that the efficiency of this ideal gas Carnot engine is given by

$$e = 1 - \frac{T_c}{T_h}. \tag{4.5}$$

An engine does not necessarily have to follow a Carnot engine cycle. All engines, however, have the same *net* effect, namely the absorption of heat from a hot reservoir, the production of work, and the discarding of heat to a cold reservoir. This leads us to ask: Do all reversible cycles operating between the same two reservoirs have the same efficiency? The answer to this question comes from the second law of thermodynamics discussed earlier: *All reversible engine cycles produce exactly the same efficiency*. Also, as you might expect, all real engines operating between two reservoirs are less efficient than reversible engines operating between the same two reservoirs. This too is a consequence of the second law of thermodynamics shown earlier.

The cycle of an ideal gas Carnot refrigerator is represented by the *pV* diagram of **Figure 4.13**. It is a Carnot engine operating in reverse. The refrigerator extracts heat Q_c from a cold-temperature reservoir at T_c when the ideal gas expands isothermally. The gas is then compressed adiabatically until its temperature reaches T_h, after which an isothermal compression of the gas results in heat Q_h being discarded to a high-temperature reservoir at T_h. Finally, the cycle is completed by an adiabatic expansion of the gas, causing its temperature to drop to T_c.

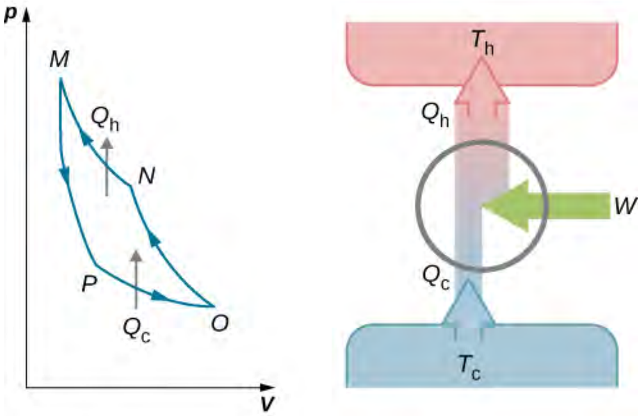


Figure 4.13 The work done on the gas in one cycle of the Carnot refrigerator is shown and given by the area enclosed by the loop *MPONM*.

The work done on the ideal gas is equal to the area enclosed by the path of the pV diagram. From the first law, this work is given by

$$W = Q_h - Q_c.$$

An analysis just like the analysis done for the Carnot engine gives

$$\frac{Q_c}{T_c} = \frac{Q_h}{T_h}.$$

When combined with **Equation 4.3**, this yields

$$K_R = \frac{T_c}{T_h - T_c} \tag{4.6}$$

for the coefficient of performance of the ideal-gas Carnot refrigerator. Similarly, we can work out the coefficient of performance for a Carnot heat pump as

$$K_P = \frac{Q_h}{Q_h - Q_c} = \frac{T_h}{T_h - T_c}. \tag{4.7}$$

We have just found equations representing the efficiency of a Carnot engine and the coefficient of performance of a Carnot refrigerator or a Carnot heat pump, assuming an ideal gas for the working substance in both devices. However, these equations are more general than their derivations imply. We will soon show that they are both valid no matter what the working substance is.

Carnot summarized his study of the Carnot engine and Carnot cycle into what is now known as **Carnot's principle**:

Carnot's Principle

No engine working between two reservoirs at constant temperatures can have a greater efficiency than a reversible engine.

This principle can be viewed as another statement of the second law of thermodynamics and can be shown to be equivalent to the Kelvin statement and the Clausius statement.

Example 4.2

The Carnot Engine

A Carnot engine has an efficiency of 0.60 and the temperature of its cold reservoir is 300 K. (a) What is the temperature of the hot reservoir? (b) If the engine does 300 J of work per cycle, how much heat is removed from the high-temperature reservoir per cycle? (c) How much heat is exhausted to the low-temperature reservoir per cycle?

Strategy

From the temperature dependence of the thermal efficiency of the Carnot engine, we can find the temperature of the hot reservoir. Then, from the definition of the efficiency, we can find the heat removed when the work done by the engine is given. Finally, energy conservation will lead to how much heat must be dumped to the cold reservoir.

Solution

a. From $e = 1 - T_c/T_h$ we have

$$0.60 = 1 - \frac{300\text{ K}}{T_h},$$

so that the temperature of the hot reservoir is

$$T_h = \frac{300\text{ K}}{1 - 0.60} = 750\text{ K}.$$

b. By definition, the efficiency of the engine is $e = W/Q$, so that the heat removed from the high-temperature reservoir per cycle is

$$Q_h = \frac{W}{e} = \frac{300\text{ J}}{0.60} = 500\text{ J}.$$

c. From the first law, the heat exhausted to the low-temperature reservoir per cycle by the engine is

$$Q_c = Q_h - W = 500\text{ J} - 300\text{ J} = 200\text{ J}.$$

Significance

A Carnot engine has the maximum possible efficiency of converting heat into work between two reservoirs, but this does not necessarily mean it is 100% efficient. As the difference in temperatures of the hot and cold reservoir increases, the efficiency of a Carnot engine increases.

Example 4.3

A Carnot Heat Pump

Imagine a Carnot heat pump operates between an outside temperature of $0\,°\text{C}$ and an inside temperature of $20.0\,°\text{C}$. What is the work needed if the heat delivered to the inside of the house is 30.0 kJ?

Strategy

Because the heat pump is assumed to be a Carnot pump, its performance coefficient is given by $K_P = Q_h/W = T_h/(T_h - T_c)$. Thus, we can find the work W from the heat delivered Q_h.

Solution

The work needed is obtained from

$$W = Q_h/K_P = Q_h(T_h - T_c)/T_h = 30\text{ kJ} \times (293\text{ K} - 273\text{ K})/293\text{ K} = 2\text{ kJ}.$$

Significance

We note that this work depends not only on the heat delivered to the house but also on the temperatures outside and inside. The dependence on the temperature outside makes them impractical to use in areas where the

> temperature is much colder outside than room temperature.

In terms of energy costs, the heat pump is a very economical means for heating buildings (**Figure 4.14**). Contrast this method with turning electrical energy directly into heat with resistive heating elements. In this case, one unit of electrical energy furnishes at most only one unit of heat. Unfortunately, heat pumps have problems that do limit their usefulness. They are quite expensive to purchase compared to resistive heating elements, and, as the performance coefficient for a Carnot heat pump shows, they become less effective as the outside temperature decreases. In fact, below about $-10\ °\text{C}$, the heat they furnish is less than the energy used to operate them.

Figure 4.14 A photograph of a heat pump (large box) located outside a house. This heat pump is located in a warm climate area, like the southern United States, since it would be far too inefficient located in the northern half of the United States. (credit: modification of work by Peter Stevens)

4.3 **Check Your Understanding** A Carnot engine operates between reservoirs at $400\ °\text{C}$ and $30\ °\text{C}$. (a) What is the efficiency of the engine? (b) If the engine does 5.0 J of work per cycle, how much heat per cycle does it absorb from the high-temperature reservoir? (c) How much heat per cycle does it exhaust to the cold-temperature reservoir? (d) What temperatures at the cold reservoir would give the minimum and maximum efficiency?

4.4 **Check Your Understanding** A Carnot refrigerator operates between two heat reservoirs whose temperatures are $0\ °\text{C}$ and $25\ °\text{C}$. (a) What is the coefficient of performance of the refrigerator? (b) If 200 J of work are done on the working substance per cycle, how much heat per cycle is extracted from the cold reservoir? (c) How much heat per cycle is discarded to the hot reservoir?

4.6 | Entropy

Learning Objectives

By the end of this section you will be able to:

- Describe the meaning of entropy
- Calculate the change of entropy for some simple processes

The second law of thermodynamics is best expressed in terms of a *change* in the thermodynamic variable known as **entropy**, which is represented by the symbol S. Entropy, like internal energy, is a state function. This means that when a system makes a transition from one state into another, the change in entropy ΔS is independent of path and depends only on the thermodynamic variables of the two states.

We first consider ΔS for a system undergoing a reversible process at a constant temperature. In this case, the change in entropy of the system is given by

$$\Delta S = \frac{Q}{T}, \tag{4.8}$$

where Q is the heat exchanged by the system kept at a temperature T (in kelvin). If the system absorbs heat—that is, with $Q > 0$—the entropy of the system increases. As an example, suppose a gas is kept at a constant temperature of 300 K while it absorbs 10 J of heat in a reversible process. Then from **Equation 4.8**, the entropy change of the gas is

$$\Delta S = \frac{10\ \text{J}}{300\ \text{K}} = 0.033\ \text{J/K}.$$

Similarly, if the gas loses 5.0 J of heat; that is, $Q = -5.0\ \text{J}$, at temperature $T = 200\ \text{K}$, we have the entropy change of the system given by

$$\Delta S = \frac{-5.0\ \text{J}}{200\ \text{K}} = -0.025\ \text{J/K}.$$

Example 4.4

Entropy Change of Melting Ice

Heat is slowly added to a 50-g chunk of ice at $0\ °\text{C}$ until it completely melts into water at the same temperature. What is the entropy change of the ice?

Strategy

Because the process is slow, we can approximate it as a reversible process. The temperature is a constant, and we can therefore use **Equation 4.8** in the calculation.

Solution

The ice is melted by the addition of heat:

$$Q = mL_\text{f} = 50\ \text{g} \times 335\ \text{J/g} = 16.8\ \text{kJ}.$$

In this reversible process, the temperature of the ice-water mixture is fixed at $0\ °\text{C}$ or 273 K. Now from $\Delta S = Q/T$, the entropy change of the ice is

$$\Delta S = \frac{16.8\ \text{kJ}}{273\ \text{K}} = 61.5\ \text{J/K}$$

when it melts to water at $0\ °\text{C}$.

Significance

During a phase change, the temperature is constant, allowing us to use **Equation 4.8** to solve this problem. The same equation could also be used if we changed from a liquid to a gas phase, since the temperature does not change during that process either.

The change in entropy of a system for an arbitrary, reversible transition for which the temperature is not necessarily constant is defined by modifying $\Delta S = Q/T$. Imagine a system making a transition from state A to B in small, discrete steps. The temperatures associated with these states are T_A and $T_B,$ respectively. During each step of the transition, the system exchanges heat ΔQ_i reversibly at a temperature $T_i.$ This can be accomplished experimentally by placing the system in thermal contact with a large number of heat reservoirs of varying temperatures T_i, as illustrated in **Figure 4.15**. The change in entropy for each step is $\Delta S_i = Q_i/T_i.$ The net change in entropy of the system for the transition is

$$\Delta S = S_B - S_A = \sum_i \Delta S_i = \sum_i \frac{\Delta Q_i}{T_i}. \tag{4.9}$$

We now take the limit as $\Delta Q_i \to 0$, and the number of steps approaches infinity. Then, replacing the summation by an integral, we obtain

$$\Delta S = S_B - S_A = \int_A^B \frac{dQ}{T}, \tag{4.10}$$

where the integral is taken between the initial state *A* and the final state *B*. This equation is valid only if the transition from *A* to *B* is reversible.

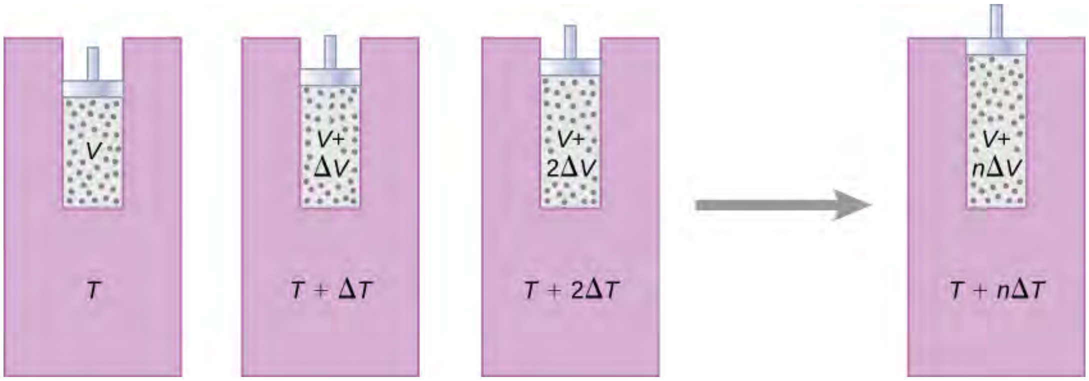


Figure 4.15 The gas expands at constant pressure as its temperature is increased in small steps through the use of a series of heat reservoirs.

As an example, let us determine the net entropy change of a reversible engine while it undergoes a single Carnot cycle. In the adiabatic steps 2 and 4 of the cycle shown in **Figure 4.11**, no heat exchange takes place, so $\Delta S_2 = \Delta S_4 = \int dQ/T = 0.$ In step 1, the engine absorbs heat Q_h at a temperature T_h, so its entropy change is $\Delta S_1 = Q_h/T_h$. Similarly, in step 3, $\Delta S_3 = -Q_c/T_c$. The net entropy change of the engine in one cycle of operation is then

$$\Delta S_E = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4 = \frac{Q_h}{T_h} - \frac{Q_c}{T_c}.$$

However, we know that for a Carnot engine,

$$\frac{Q_h}{T_h} = \frac{Q_c}{T_c},$$

so

$$\Delta S_E = 0.$$

There is no net change in the entropy of the Carnot engine over a complete cycle. Although this result was obtained for a particular case, its validity can be shown to be far more general: There is no net change in the entropy of a system undergoing any complete reversible cyclic process. Mathematically, we write this statement as

$$\oint dS = \oint \frac{dQ}{T} = 0 \tag{4.11}$$

where $\oint$ represents the integral over a *closed reversible path*.

We can use **Equation 4.11** to show that the entropy change of a system undergoing a reversible process between two given states is path independent. An arbitrary, closed path for a reversible cycle that passes through the states A and B is shown in **Figure 4.16**. From **Equation 4.11**, $\oint dS = 0$ for this closed path. We may split this integral into two segments, one along I, which leads from A to B, the other along II, which leads from B to A. Then

$$\left[\int_A^B dS\right]_{\text{I}} + \left[\int_B^A dS\right]_{\text{II}} = 0.$$

Since the process is reversible,

$$\left[\int_A^B dS\right]_{\text{I}} = \left[\int_A^B dS\right]_{\text{II}}.$$

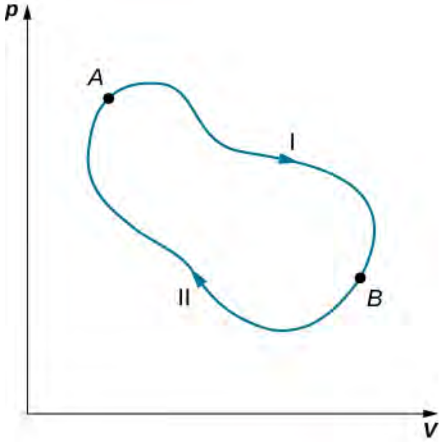


Figure 4.16 The closed loop passing through states A and B represents a reversible cycle.

Hence, the entropy change in going from A to B is the same for paths I and II. Since paths I and II are arbitrary, reversible paths, the entropy change in a transition between two equilibrium states is the same for all the reversible processes joining these states. Entropy, like internal energy, is therefore a state function.

What happens if the process is irreversible? When the process is irreversible, we expect the entropy of a closed system, or the system and its environment (the universe), to increase. Therefore we can rewrite this expression as

$$\Delta S \geq 0, \tag{4.12}$$

where S is the total entropy of the closed system or the entire universe, and the equal sign is for a reversible process. The fact is the **entropy statement of the second law of thermodynamics**:

Second Law of Thermodynamics (Entropy statement)

The entropy of a closed system and the entire universe never decreases.

We can show that this statement is consistent with the Kelvin statement, the Clausius statement, and the Carnot principle.

Example 4.5

Entropy Change of a System during an Isobaric Process

Determine the entropy change of an object of mass m and specific heat c that is cooled rapidly (and irreversibly) at constant pressure from T_h to T_c.

Strategy

The process is clearly stated as an irreversible process; therefore, we cannot simply calculate the entropy change from the actual process. However, because entropy of a system is a function of state, we can imagine a reversible process that starts from the same initial state and ends at the given final state. Then, the entropy change of the system is given by **Equation 4.10**, $\Delta S = \int_A^B dQ/T$.

Solution

To replace this rapid cooling with a process that proceeds reversibly, we imagine that the hot object is put into thermal contact with successively cooler heat reservoirs whose temperatures range from T_h to T_c. Throughout the substitute transition, the object loses infinitesimal amounts of heat dQ, so we have

$$\Delta S = \int_{T_\text{h}}^{T_\text{c}} \frac{dQ}{T}.$$

From the definition of heat capacity, an infinitesimal exchange dQ for the object is related to its temperature change dT by

$$dQ = mc\,dT.$$

Substituting this dQ into the expression for ΔS, we obtain the entropy change of the object as it is cooled at constant pressure from T_h to T_c :

$$\Delta S = \int_{T_\text{h}}^{T_\text{c}} \frac{mc\,dT}{T} = mc\ln\frac{T_\text{c}}{T_\text{h}}.$$

Note that $\Delta S < 0$ here because $T_\text{c} < T_\text{h}$. In other words, the object has lost some entropy. But if we count whatever is used to remove the heat from the object, we would still end up with $\Delta S_\text{universe} > 0$ because the process is irreversible.

Significance

If the temperature changes during the heat flow, you must keep it inside the integral to solve for the change in entropy. If, however, the temperature is constant, you can simply calculate the entropy change as the heat flow divided by the temperature.

Example 4.6

Stirling Engine

The steps of a reversible Stirling engine are as follows. For this problem, we will use 0.0010 mol of a monatomic gas that starts at a temperature of $133\,°\text{C}$ and a volume of $0.10\,\text{m}^3$, which will be called point *A*. Then it goes through the following steps:

1. Step *AB*: isothermal expansion at $133\,°\text{C}$ from $0.10\,\text{m}^3$ to $0.20\,\text{m}^3$
2. Step *BC*: isochoric cooling to $33\,°\text{C}$
3. Step *CD*: isothermal compression at $33\,°\text{C}$ from $0.20\,\text{m}^3$ to $0.10\,\text{m}^3$
4. Step *DA*: isochoric heating back to $133\,°\text{C}$ and $0.10\,\text{m}^3$

(a) Draw the *pV* diagram for the Stirling engine with proper labels.

(b) Fill in the following table.

Step	*W* (J)	*Q* (J)	ΔS (J/K)
Step *AB*			
Step *BC*			
Step *CD*			
Step *DA*			
Complete cycle			

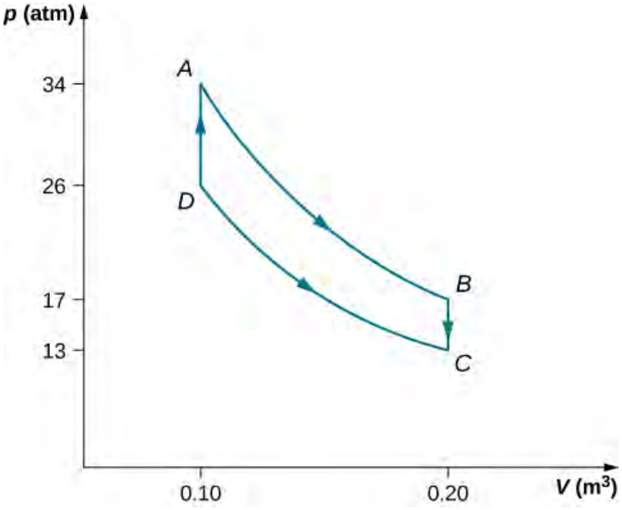
(c) How does the efficiency of the Stirling engine compare to the Carnot engine working within the same two heat reservoirs?

Strategy

Using the ideal gas law, calculate the pressure at each point so that they can be labeled on the *pV* diagram. Isothermal work is calculated using $W = nRT\ln\left(\frac{V_2}{V_1}\right)$, and an isochoric process has no work done. The heat flow is calculated from the first law of thermodynamics, $Q = \Delta E_{\text{int}} - W$ where $\Delta E_{\text{int}} = \frac{3}{2}nR\Delta T$ for monatomic gasses. Isothermal steps have a change in entropy of *Q*/*T*, whereas isochoric steps have $\Delta S = \frac{3}{2}nR\ln\left(\frac{T_2}{T_1}\right)$. The efficiency of a heat engine is calculated by using $e_{\text{Stir}} = W/Q_{\text{h}}$.

Solution

a. The graph is shown below.



b. The completed table is shown below.

Step	*W* (J)	*Q* (J)	ΔS (J/K)
Step *AB* Isotherm	2.3	2.3	0.0057
Step *BC* Isochoric	0	–1.2	0.0035
Step *CD* Isotherm	–1.8	–1.8	–0.0059
Step *DA* Isochoric	0	1.2	–0.0035
Complete cycle	0.5	0.5	~ 0

c. The efficiency of the Stirling heat engine is

$$e_{\text{Stir}} = W/Q_{\text{h}} = (Q_{AB} + Q_{CD})/(Q_{AB} + Q_{DA}) = 0.5/4.5 = 0.11.$$

If this were a Carnot engine operating between the same heat reservoirs, its efficiency would be

$$e_{\text{Car}} = 1 - \left(\frac{T_{\text{c}}}{T_{\text{h}}}\right) = 0.25.$$

Therefore, the Carnot engine would have a greater efficiency than the Stirling engine.

Significance

In the early days of steam engines, accidents would occur due to the high pressure of the steam in the boiler. Robert Stirling developed an engine in 1816 that did not use steam and therefore was safer. The Stirling engine was commonly used in the nineteenth century, but developments in steam and internal combustion engines have made it difficult to broaden the use of the Stirling engine.

The Stirling engine uses compressed air as the working substance, which passes back and forth between two chambers with a porous plug, called the regenerator, which is made of material that does not conduct heat as well. In two of the steps, pistons in the two chambers move in phase.

4.7 | Entropy on a Microscopic Scale

Learning Objectives

By the end of this section you will be able to:

- Interpret the meaning of entropy at a microscopic scale
- Calculate a change in entropy for an irreversible process of a system and contrast with the change in entropy of the universe
- Explain the third law of thermodynamics

We have seen how entropy is related to heat exchange at a particular temperature. In this section, we consider entropy from a statistical viewpoint. Although the details of the argument are beyond the scope of this textbook, it turns out that entropy can be related to how disordered or randomized a system is—the more it is disordered, the higher is its entropy. For example, a new deck of cards is very ordered, as the cards are arranged numerically by suit. In shuffling this new deck, we randomize the arrangement of the cards and therefore increase its entropy (**Figure 4.17**). Thus, by picking one card off the top of the deck, there would be no indication of what the next selected card will be.

Figure 4.17 The entropy of a new deck of cards goes up after the dealer shuffles them. (credit: “Rommel SK”/YouTube)

The second law of thermodynamics requires that the entropy of the universe increase in any irreversible process. Thus, in terms of order, the second law may be stated as follows:

In any irreversible process, the universe becomes more disordered. For example, the irreversible free expansion of an ideal gas, shown in **Figure 4.2**, results in a larger volume for the gas molecules to occupy. A larger volume means more possible arrangements for the same number of atoms, so disorder is also increased. As a result, the entropy of the gas has gone up. The gas in this case is a closed system, and the process is irreversible. Changes in phase also illustrate the connection between entropy and **disorder**.

Example 4.7

Entropy Change of the Universe

Suppose we place 50 g of ice at $0\,°\text{C}$ in contact with a heat reservoir at $20\,°\text{C}$. Heat spontaneously flows from the reservoir to the ice, which melts and eventually reaches a temperature of $20\,°\text{C}$. Find the change in entropy of (a) the ice and (b) the universe.

Strategy

Because the entropy of a system is a function of its state, we can imagine two reversible processes for the ice: (1) ice is melted at $0\,°\text{C}(T_A)$; and (2) melted ice (water) is warmed up from $0\,°\text{C}$ to $20\,°\text{C}(T_B)$ under constant pressure. Then, we add the change in entropy of the reservoir when we calculate the change in entropy of the universe.

Solution

a. From **Equation 4.10**, the increase in entropy of the ice is

$$\begin{aligned}\Delta S_{\text{ice}} &= \Delta S_1 + \Delta S_2 \\ &= \frac{mL_f}{T_A} + mc\int_A^B \frac{dT}{T} \\ &= \left(\frac{50 \times 335}{273} + 50 \times 4.19 \times \ln\frac{293}{273}\right)\text{J/K} \\ &= 76.3\ \text{J/K}.\end{aligned}$$

b. During this transition, the reservoir gives the ice an amount of heat equal to

$$\begin{aligned}Q &= mL_f + mc(T_B - T_A) \\ &= 50 \times (335 + 4.19 \times 20)\ \text{J} \\ &= 2.10 \times 10^4\ \text{J}.\end{aligned}$$

This leads to a change (decrease) in entropy of the reservoir:

$$\Delta S_{\text{reservoir}} = \frac{-Q}{T_B} = -71.7\ \text{J/K}.$$

The increase in entropy of the universe is therefore

$$\Delta S_{\text{universe}} = 76.3\ \text{J/K} - 71.7\ \text{J/K} = 4.6\ \text{J/K} > 0.$$

Significance

The entropy of the universe therefore is greater than zero since the ice gains more entropy than the reservoir loses. If we considered only the phase change of the ice into water and not the temperature increase, the entropy change of the ice and reservoir would be the same, resulting in the universe gaining no entropy.

This process also results in a more disordered universe. The ice changes from a solid with molecules located at specific sites to a liquid whose molecules are much freer to move. The molecular arrangement has therefore become more randomized. Although the change in average kinetic energy of the molecules of the heat reservoir is negligible, there is nevertheless a significant decrease in the entropy of the reservoir because it has many more molecules than the melted ice cube. However, the reservoir's decrease in entropy is still not as large as the increase in entropy of the ice. The increased disorder of the ice more than compensates for the increased order of the reservoir, and the entropy of the universe increases by 4.6 J/K.

You might suspect that the growth of different forms of life might be a net ordering process and therefore a violation of the second law. After all, a single cell gathers molecules and eventually becomes a highly structured organism, such as a human being. However, this ordering process is more than compensated for by the disordering of the rest of the universe. The net result is an increase in entropy and an increase in the disorder of the universe.

4.5 Check Your Understanding In **Example 4.7**, the spontaneous flow of heat from a hot object to a cold object results in a net increase in entropy of the universe. Discuss how this result can be related to an increase in disorder of the system.

The second law of thermodynamics makes clear that the entropy of the universe never decreases during any thermodynamic process. For any other thermodynamic system, when the process is reversible, the change of the entropy is given by $\Delta S = Q/T$. But what happens if the temperature goes to zero, $T \to 0$? It turns out this is not a question that can be answered by the second law.

A fundamental issue still remains: Is it possible to cool a system all the way down to zero kelvin? We understand that the system must be at its lowest energy state because lowering temperature reduces the kinetic energy of the constituents in the system. What happens to the entropy of a system at the absolute zero temperature? It turns out the absolute zero temperature is not reachable—at least, not though a finite number of cooling steps. This is a statement of the **third law of thermodynamics**, whose proof requires quantum mechanics that we do not present here. In actual experiments, physicists have continuously pushed that limit downward, with the lowest temperature achieved at about 1×10^{-10} K in a low-temperature lab at the Helsinki University of Technology in 2008.

Like the second law of thermodynamics, the third law of thermodynamics can be stated in different ways. One of the common statements of the third law of thermodynamics is: *The absolute zero temperature cannot be reached through any finite number of cooling steps*.

In other words, the temperature of any given physical system must be finite, that is, $T > 0$. This produces a very interesting question in physics: Do we know how a system would behave if it were at the absolute zero temperature?

The reason a system is unable to reach 0 K is fundamental and requires quantum mechanics to fully understand its origin. But we can certainly ask what happens to the entropy of a system when we try to cool it down to 0 K. Because the amount of heat that can be removed from the system becomes vanishingly small, we expect that the change in entropy of the system along an isotherm approaches zero, that is,

$$\lim_{T \to 0} (\Delta S)_T = 0. \tag{4.13}$$

This can be viewed as another statement of the third law, with all the isotherms becoming **isentropic**, or into a reversible ideal adiabat. We can put this expression in words: *A system becomes perfectly ordered when its temperature approaches absolute zero and its entropy approaches its absolute minimum*.

The third law of thermodynamics puts another limit on what can be done when we look for energy resources. If there could be a reservoir at the absolute zero temperature, we could have engines with efficiency of 100%, which would, of course, violate the second law of thermodynamics.

Example 4.8

Entropy Change of an Ideal Gas in Free Expansion

An ideal gas occupies a partitioned volume V_1 inside a box whose walls are thermally insulating, as shown in **Figure 4.18**(a). When the partition is removed, the gas expands and fills the entire volume V_2 of the box, as shown in part (b). What is the entropy change of the universe (the system plus its environment)?

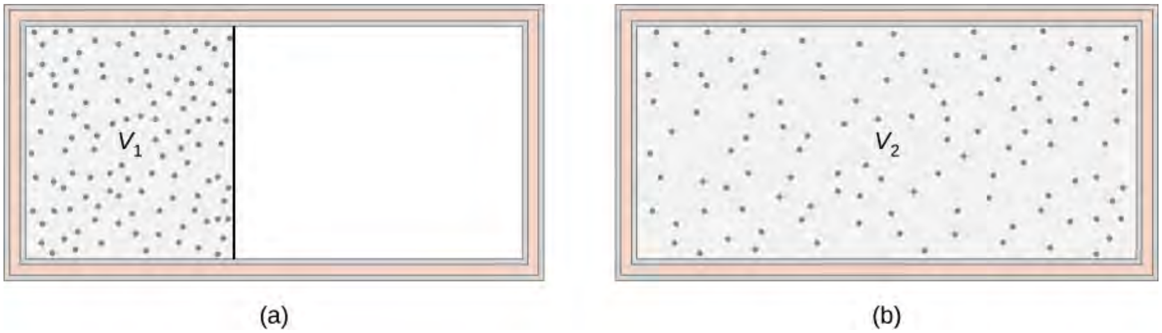


Figure 4.18 The adiabatic free expansion of an ideal gas from volume V_1 to volume V_2.

Strategy

The adiabatic free expansion of an ideal gas is an irreversible process. There is no change in the internal energy (and hence temperature) of the gas in such an expansion because no work or heat transfer has happened. Thus, a convenient reversible path connecting the same two equilibrium states is a slow, isothermal expansion from V_1 to V_2. In this process, the gas could be expanding against a piston while in thermal contact with a heat reservoir, as in step 1 of the Carnot cycle.

Solution

Since the temperature is constant, the entropy change is given by $\Delta S = Q/T$, where

$$Q = W = \int_{V_1}^{V_2} p dV$$

because $\Delta E_{\text{int}} = 0$. Now, with the help of the ideal gas law, we have

$$Q = nRT \int_{V_1}^{V_2} \frac{dV}{V} = nRT \ln\frac{V_2}{V_1},$$

so the change in entropy of the gas is

$$\Delta S = \frac{Q}{T} = nR \ln\frac{V_2}{V_1}.$$

Because $V_2 > V_1$, ΔS is positive, and the entropy of the gas has gone up during the free expansion.

Significance

What about the environment? The walls of the container are thermally insulating, so no heat exchange takes place between the gas and its surroundings. The entropy of the environment is therefore constant during the expansion. The net entropy change of the universe is then simply the entropy change of the gas. Since this is positive, the entropy of the universe increases in the free expansion of the gas.

Example 4.9

Entropy Change during Heat Transfer

Heat flows from a steel object of mass 4.00 kg whose temperature is 400 K to an identical object at 300 K. Assuming that the objects are thermally isolated from the environment, what is the net entropy change of the universe after thermal equilibrium has been reached?

Strategy

Since the objects are identical, their common temperature at equilibrium is 350 K. To calculate the entropy changes associated with their transitions, we substitute the irreversible process of the heat transfer by two isobaric, reversible processes, one for each of the two objects. The entropy change for each object is then given by $\Delta S = mc\ln(T_B/T_A)$.

Solution

Using $c = 450\ \text{J/kg}\cdot\text{K}$, the specific heat of steel, we have for the hotter object

$$\begin{aligned}\Delta S_\text{h} &= \int_{T_1}^{T_2} \frac{mc\,dT}{T} = mc\ln\frac{T_2}{T_1} \\ &= (4.00\ \text{kg})(450\ \text{J/kg}\cdot\text{K})\ln\frac{350\ \text{K}}{400\ \text{K}} = -240\ \text{J/K}.\end{aligned}$$

Similarly, the entropy change of the cooler object is

$$\Delta S_\text{c} = (4.00\ \text{kg})(450\ \text{J/kg}\cdot\text{K})\ln\frac{350\ \text{K}}{300\ \text{K}} = 277\ \text{J/K}.$$

The net entropy change of the two objects during the heat transfer is then

$$\Delta S_\text{h} + \Delta S_\text{c} = 37\ \text{J/K}.$$

Significance

The objects are thermally isolated from the environment, so its entropy must remain constant. Thus, the entropy of the universe also increases by 37 J/K.

4.6 Check Your Understanding A quantity of heat Q is absorbed from a reservoir at a temperature T_h by a cooler reservoir at a temperature T_c. What is the entropy change of the hot reservoir, the cold reservoir, and the universe?

4.7 Check Your Understanding A 50-g copper piece at a temperature of $20\ °\text{C}$ is placed into a large insulated vat of water at $100\ °\text{C}$. (a) What is the entropy change of the copper piece when it reaches thermal equilibrium with the water? (b) What is the entropy change of the water? (c) What is the entropy change of the universe?

View this **site (https://openstaxcollege.org/l/21reversereact)** to learn about entropy and microstates. Start with a large barrier in the middle and 1000 molecules in only the left chamber. What is the total entropy of the system? Now remove the barrier and let the molecules travel from the left to the right hand side? What is the total entropy of the system now? Lastly, add heat and note what happens to the temperature. Did this increase entropy of the system?

CHAPTER 4 REVIEW

KEY TERMS

Carnot cycle cycle that consists of two isotherms at the temperatures of two reservoirs and two adiabatic processes connecting the isotherms

Carnot engine Carnot heat engine, refrigerator, or heat pump that operates on a Carnot cycle

Carnot principle principle governing the efficiency or performance of a heat device operating on a Carnot cycle: any reversible heat device working between two reservoirs must have the same efficiency or performance coefficient, greater than that of an irreversible heat device operating between the same two reservoirs

Clausius statement of the second law of thermodynamics heat never flows spontaneously from a colder object to a hotter object

coefficient of performance measure of effectiveness of a refrigerator or heat pump

cold reservoir sink of heat used by a heat engine

disorder measure of order in a system; the greater the disorder is, the higher the entropy

efficiency (*e*) output work from the engine over the input heat to the engine from the hot reservoir

entropy state function of the system that changes when heat is transferred between the system and the environment

entropy statement of the second law of thermodynamics entropy of a closed system or the entire universe never decreases

heat engine device that converts heat into work

heat pump device that delivers heat to a hot reservoir

hot reservoir source of heat used by a heat engine

irreversibility phenomenon associated with a natural process

irreversible process process in which neither the system nor its environment can be restored to their original states at the same time

isentropic reversible adiabatic process where the process is frictionless and no heat is transferred

Kelvin statement of the second law of thermodynamics it is impossible to convert the heat from a single source into work without any other effect

perfect engine engine that can convert heat into work with 100% efficiency

perfect refrigerator (heat pump) refrigerator (heat pump) that can remove (dump) heat without any input of work

refrigerator device that removes heat from a cold reservoir

reversible process process in which both the system and the external environment theoretically can be returned to their original states

third law of thermodynamics absolute zero temperature cannot be reached through any finite number of cooling steps

KEY EQUATIONS

Result of energy conservation	$W = Q_\text{h} - Q_\text{c}$
Efficiency of a heat engine	$e = \frac{W}{Q_\text{h}} = 1 - \frac{Q_\text{c}}{Q_\text{h}}$
Coefficient of performance of a refrigerator	$K_\text{R} = \frac{Q_\text{c}}{W} = \frac{Q_\text{c}}{Q_\text{h} - Q_\text{c}}$

Coefficient of performance of a heat pump	$K_P = \frac{Q_h}{W} = \frac{Q_h}{Q_h - Q_c}$
Resulting efficiency of a Carnot cycle	$e = 1 - \frac{T_c}{T_h}$
Performance coefficient of a reversible refrigerator	$K_R = \frac{T_c}{T_h - T_c}$
Performance coefficient of a reversible heat pump	$K_P = \frac{T_h}{T_h - T_c}$
Entropy of a system undergoing a reversible process at a constant temperature	$\Delta S = \frac{Q}{T}$
Change of entropy of a system under a reversible process	$\Delta S = S_B - S_A = \int_A^B dQ/T$
Entropy of a system undergoing any complete reversible cyclic process	$\oint dS = \oint \frac{dQ}{T} = 0$
Change of entropy of a closed system under an irreversible process	$\Delta S \geq 0$
Change in entropy of the system along an isotherm	$\lim_{T \to 0} (\Delta S)_T = 0$

SUMMARY

4.1 Reversible and Irreversible Processes

- A reversible process is one in which both the system and its environment can return to exactly the states they were in by following the reverse path.
- An irreversible process is one in which the system and its environment cannot return together to exactly the states that they were in.
- The irreversibility of any natural process results from the second law of thermodynamics.

4.2 Heat Engines

- The work done by a heat engine is the difference between the heat absorbed from the hot reservoir and the heat discharged to the cold reservoir, that is, $W = Q_h - Q_c$.
- The ratio of the work done by the engine and the heat absorbed from the hot reservoir provides the efficiency of the engine, that is, $e = W/Q_h = 1 - Q_c/Q_h$.

4.3 Refrigerators and Heat Pumps

- A refrigerator or a heat pump is a heat engine run in reverse.
- The focus of a refrigerator is on removing heat from the cold reservoir with a coefficient of performance K_R.
- The focus of a heat pump is on dumping heat to the hot reservoir with a coefficient of performance K_P.

4.4 Statements of the Second Law of Thermodynamics

- The Kelvin statement of the second law of thermodynamics: It is impossible to convert the heat from a single source into work without any other effect.
- The Kelvin statement and Clausius statement of the second law of thermodynamics are equivalent.

4.5 The Carnot Cycle

- The Carnot cycle is the most efficient engine for a reversible cycle designed between two reservoirs.
- The Carnot principle is another way of stating the second law of thermodynamics.

4.6 Entropy

- The change in entropy for a reversible process at constant temperature is equal to the heat divided by the temperature. The entropy change of a system under a reversible process is given by $\Delta S = \int_A^B dQ/T$.
- A system's change in entropy between two states is independent of the reversible thermodynamic path taken by the system when it makes a transition between the states.

4.7 Entropy on a Microscopic Scale

- Entropy can be related to how disordered a system is—the more it is disordered, the higher is its entropy. In any irreversible process, the universe becomes more disordered.
- According to the third law of thermodynamics, absolute zero temperature is unreachable.

CONCEPTUAL QUESTIONS

4.1 Reversible and Irreversible Processes

1. State an example of a process that occurs in nature that is as close to reversible as it can be.

4.2 Heat Engines

2. Explain in practical terms why efficiency is defined as W/Q_{h}.

4.3 Refrigerators and Heat Pumps

3. If the refrigerator door is left open, what happens to the temperature of the kitchen?

4. Is it possible for the efficiency of a reversible engine to be greater than 1.0? Is it possible for the coefficient of performance of a reversible refrigerator to be less than 1.0?

4.4 Statements of the Second Law of Thermodynamics

5. In the text, we showed that if the Clausius statement is false, the Kelvin statement must also be false. Now show the reverse, such that if the Kelvin statement is false, it follows that the Clausius statement is false.

6. Why don't we operate ocean liners by extracting heat from the ocean or operate airplanes by extracting heat from the atmosphere?

7. Discuss the practical advantages and disadvantages of heat pumps and electric heating.

8. The energy output of a heat pump is greater than the energy used to operate the pump. Why doesn't this statement violate the first law of thermodynamics?

9. Speculate as to why nuclear power plants are less efficient than fossil-fuel plants based on temperature arguments.

10. An ideal gas goes from state $(p_{\text{i}}, V_{\text{i}})$ to state $(p_{\text{f}}, V_{\text{f}})$ when it is allowed to expand freely. Is it possible to represent the actual process on a pV diagram? Explain.

4.5 The Carnot Cycle

11. To increase the efficiency of a Carnot engine, should the temperature of the hot reservoir be raised or lowered? What about the cold reservoir?

12. How could you design a Carnot engine with 100% efficiency?

13. What type of processes occur in a Carnot cycle?

4.6 Entropy

14. Does the entropy increase for a Carnot engine for each cycle?

15. Is it possible for a system to have an entropy change if it neither absorbs nor emits heat during a reversible transition? What happens if the process is irreversible?

4.7 Entropy on a Microscopic Scale

16. Are the entropy changes of the *systems* in the following processes positive or negative? (a) *water vapor* that condenses on a cold surface; (b) gas in a container that leaks into the surrounding atmosphere; (c) an *ice cube* that melts in a glass of lukewarm water; (d) the *lukewarm water* of part (c); (e) a *real heat engine* performing a cycle; (f) *food* cooled in a refrigerator.

17. Discuss the entropy changes in the systems of Question 21.10 in terms of disorder.

PROBLEMS

4.1 Reversible and Irreversible Processes

18. A tank contains 111.0 g chlorine gas (Cl_2), which is at temperature $82.0\,°C$ and absolute pressure 5.70×10^5 Pa. The temperature of the air outside the tank is $20.0\,°C$. The molar mass of Cl_2 is 70.9 g/mol. (a) What is the volume of the tank? (b) What is the internal energy of the gas? (c) What is the work done by the gas if the temperature and pressure inside the tank drop to $31.0\,°C$ and 3.80×10^5 Pa, respectively, due to a leak?

19. A mole of ideal monatomic gas at $0\,°C$ and 1.00 atm is warmed up to expand isobarically to triple its volume. How much heat is transferred during the process?

20. A mole of an ideal gas at pressure 4.00 atm and temperature 298 K expands isothermally to double its volume. What is the work done by the gas?

21. After a free expansion to quadruple its volume, a mole of ideal diatomic gas is compressed back to its original volume isobarically and then cooled down to its original temperature. What is the minimum heat removed from the gas in the final step to restoring its state?

4.2 Heat Engines

22. An engine is found to have an efficiency of 0.40. If it does 200 J of work per cycle, what are the corresponding quantities of heat absorbed and rejected?

23. In performing 100.0 J of work, an engine rejects 50.0 J of heat. What is the efficiency of the engine?

24. An engine with an efficiency of 0.30 absorbs 500 J of heat per cycle. (a) How much work does it perform per cycle? (b) How much heat does it reject per cycle?

25. It is found that an engine rejects 100.0 J while absorbing 125.0 J each cycle of operation. (a) What is the efficiency of the engine? (b) How much work does it perform per cycle?

26. The temperature of the cold reservoir of the engine is 300 K. It has an efficiency of 0.30 and absorbs 500 J of heat per cycle. (a) How much work does it perform per cycle? (b) How much heat does it reject per cycle?

27. The Kelvin temperature of the hot reservoir of an engine is twice that of the cold reservoir, and work done by the engine per cycle is 50 J. Calculate (a) the efficiency of the engine, (b) the heat absorbed per cycle, and (c) the heat rejected per cycle.

28. A coal power plant consumes 100,000 kg of coal per hour and produces 500 MW of power. If the heat of combustion of coal is 30 MJ/kg, what is the efficiency of the power plant?

4.3 Refrigerators and Heat Pumps

29. A refrigerator has a coefficient of performance of 3.0. (a) If it requires 200 J of work per cycle, how much heat per cycle does it remove the cold reservoir? (b) How much heat per cycle is discarded to the hot reservoir?

30. During one cycle, a refrigerator removes 500 J from a cold reservoir and rejects 800 J to its hot reservoir. (a) What is its coefficient of performance? (b) How much work per cycle does it require to operate?

31. If a refrigerator discards 80 J of heat per cycle and its coefficient of performance is 6.0, what are (a) the quantity off heat it removes per cycle from a cold reservoir and (b) the amount of work per cycle required for its operation?

32. A refrigerator has a coefficient of performance of 3.0. (a) If it requires 200 J of work per cycle, how much heat per cycle does it remove the cold reservoir? (b) How much heat per cycle is discarded to the hot reservoir?

4.5 The Carnot Cycle

33. The temperature of the cold and hot reservoirs between which a Carnot refrigerator operates are $-73\,°C$ and $270\,°C$, respectively. Which is its coefficient of performance?

34. Suppose a Carnot refrigerator operates between T_c and T_h. Calculate the amount of work required to extract 1.0 J of heat from the cold reservoir if (a) $T_c = 7\,°C$, $T_h = 27\,°C$; (b) $T_c = -73\,°C$, $T_h = 27\,°C$; (c) $T_c = -173\,°C$, $T_h = 27\,°C$; and (d) $T_c = -273\,°C$, $T_h = 27\,°C$.

35. A Carnot engine operates between reservoirs at 600 and 300 K. If the engine absorbs 100 J per cycle at the hot reservoir, what is its work output per cycle?

36. A 500-W motor operates a Carnot refrigerator between $-5\,°C$ and $30\,°C$. (a) What is the amount of heat per second extracted from the inside of the refrigerator? (b) How much heat is exhausted to the outside air per second?

37. Sketch a Carnot cycle on a temperature-volume diagram.

38. A Carnot heat pump operates between $0\,°C$ and $20\,°C$. How much heat is exhausted into the interior of a house for every 1.0 J of work done by the pump?

39. An engine operating between heat reservoirs at $20\,°C$ and $200\,°C$ extracts 1000 J per cycle from the hot reservoir. (a) What is the maximum possible work that engine can do per cycle? (b) For this maximum work, how much heat is exhausted to the cold reservoir per cycle?

40. Suppose a Carnot engine can be operated between two reservoirs as either a heat engine or a refrigerator. How is the coefficient of performance of the refrigerator related to the efficiency of the heat engine?

41. A Carnot engine is used to measure the temperature of a heat reservoir. The engine operates between the heat reservoir and a reservoir consisting of water at its triple point. (a) If 400 J per cycle are removed from the heat reservoir while 200 J per cycle are deposited in the triple-point reservoir, what is the temperature of the heat reservoir? (b) If 400 J per cycle are removed from the triple-point reservoir while 200 J per cycle are deposited in the heat reservoir, what is the temperature of the heat reservoir?

42. What is the minimum work required of a refrigerator if it is to extract 50 J per cycle from the inside of a freezer at $-10\,°C$ and exhaust heat to the air at $25\,°C$?

4.6 Entropy

43. Two hundred joules of heat are removed from a heat reservoir at a temperature of 200 K. What is the entropy change of the reservoir?

44. In an isothermal reversible expansion at $27\,°C$, an ideal gas does 20 J of work. What is the entropy change of the gas?

45. An ideal gas at 300 K is compressed isothermally to one-fifth its original volume. Determine the entropy change per mole of the gas.

46. What is the entropy change of 10 g of steam at $100\,°C$ when it condenses to water at the same temperature?

47. A metal rod is used to conduct heat between two reservoirs at temperatures T_h and T_c, respectively. When an amount of heat Q flows through the rod from the hot to the cold reservoir, what is the net entropy change of the rod, the hot reservoir, the cold reservoir, and the universe?

48. For the Carnot cycle of **Figure 4.12**, what is the entropy change of the hot reservoir, the cold reservoir, and the universe?

49. A 5.0-kg piece of lead at a temperature of $600\,°C$ is placed in a lake whose temperature is $15\,°C$. Determine the entropy change of (a) the lead piece, (b) the lake, and (c) the universe.

50. One mole of an ideal gas doubles its volume in a reversible isothermal expansion. (a) What is the change in entropy of the gas? (b) If 1500 J of heat are added in this process, what is the temperature of the gas?

51. One mole of an ideal monatomic gas is confined to a rigid container. When heat is added reversibly to the gas, its temperature changes from T_1 to T_2. (a) How much heat is added? (b) What is the change in entropy of the gas?

52. (a) A 5.0-kg rock at a temperature of $20\,°C$ is dropped into a shallow lake also at $20\,°C$ from a height of 1.0×10^3 m. What is the resulting change in entropy of the universe? (b) If the temperature of the rock is $100\,°C$ when it is dropped, what is the change of entropy of the universe? Assume that air friction is negligible (not a good assumption) and that $c = 860\,\text{J/kg} \cdot \text{K}$ is the specific heat of the rock.

4.7 Entropy on a Microscopic Scale

53. A copper rod of cross-sectional area $5.0\,\text{cm}^2$ and length 5.0 m conducts heat from a heat reservoir at 373 K to one at 273 K. What is the time rate of change of the universe's entropy for this process?

54. Fifty grams of water at $20\,°\text{C}$ is heated until it becomes vapor at $100\,°\text{C}$. Calculate the change in entropy of the water in this process.

55. Fifty grams of water at $0\,°\text{C}$ are changed into vapor at $100\,°\text{C}$. What is the change in entropy of the water in this process?

56. In an isochoric process, heat is added to 10 mol of monoatomic ideal gas whose temperature increases from 273 to 373 K. What is the entropy change of the gas?

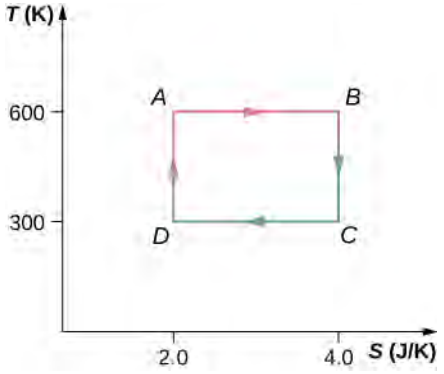
57. Two hundred grams of water at $0\,°\text{C}$ is brought into contact with a heat reservoir at $80\,°\text{C}$. After thermal equilibrium is reached, what is the temperature of the water? Of the reservoir? How much heat has been transferred in the process? What is the entropy change of the water? Of the reservoir? What is the entropy change of the universe?

58. Suppose that the temperature of the water in the previous problem is raised by first bringing it to thermal equilibrium with a reservoir at a temperature of $40\,°\text{C}$ and then with a reservoir at $80\,°\text{C}$. Calculate the entropy changes of (a) each reservoir, (b) of the water, and (c) of the universe.

59. Two hundred grams of water at $0\,°\text{C}$ is brought into contact into thermal equilibrium successively with reservoirs at $20\,°\text{C}$, $40\,°\text{C}$, $60\,°\text{C}$, and $80\,°\text{C}$. (a) What is the entropy change of the water? (b) Of the reservoir? (c) What is the entropy change of the universe?

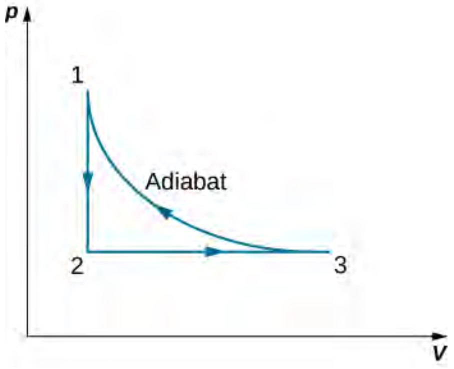
60. (a) Ten grams of H_2O starts as ice at $0\,°\text{C}$. The ice absorbs heat from the air (just above $0\,°\text{C}$) until all of it melts. Calculate the entropy change of the H_2O, of the air, and of the universe. (b) Suppose that the air in part (a) is at $20\,°\text{C}$ rather than $0\,°\text{C}$ and that the ice absorbs heat until it becomes water at $20\,°\text{C}$. Calculate the entropy change of the H_2O, of the air, and of the universe. (c) Is either of these processes reversible?

61. The Carnot cycle is represented by the temperature-entropy diagram shown below. (a) How much heat is absorbed per cycle at the high-temperature reservoir? (b) How much heat is exhausted per cycle at the low-temperature reservoir? (c) How much work is done per cycle by the engine? (d) What is the efficiency of the engine?



62. A Carnot engine operating between heat reservoirs at 500 and 300 K absorbs 1500 J per cycle at the high-temperature reservoir. (a) Represent the engine's cycle on a temperature-entropy diagram. (b) How much work per cycle is done by the engine?

63. A monoatomic ideal gas (*n* moles) goes through a cyclic process shown below. Find the change in entropy of the gas in each step and the total entropy change over the entire cycle.



64. A Carnot engine has an efficiency of 0.60. When the temperature of its cold reservoir changes, the efficiency drops to 0.55. If initially $T_c = 27\,°\text{C}$, determine (a) the constant value of T_h and (b) the final value of T_c.

65. A Carnot engine performs 100 J of work while rejecting 200 J of heat each cycle. After the temperature of the hot reservoir only is adjusted, it is found that the engine now does 130 J of work while discarding the same quantity of heat. (a) What are the initial and final efficiencies of the engine? (b) What is the fractional change in the temperature of the hot reservoir?

66. A Carnot refrigerator exhausts heat to the air, which is at a temperature of $25\,°\text{C}$. How much power is used by the refrigerator if it freezes 1.5 g of water per second? Assume the water is at $0\,°\text{C}$.

ADDITIONAL PROBLEMS

67. A 300-W heat pump operates between the ground, whose temperature is $0\,°\text{C}$, and the interior of a house at $22\,°\text{C}$. What is the maximum amount of heat per hour that the heat pump can supply to the house?

68. An engineer must design a refrigerator that does 300 J of work per cycle to extract 2100 J of heat per cycle from a freezer whose temperature is $-10\,°\text{C}$. What is the maximum air temperature for which this condition can be met? Is this a reasonable condition to impose on the design?

69. A Carnot engine employs 1.5 mol of nitrogen gas as a working substance, which is considered as an ideal diatomic gas with $\gamma = 7.5$ at the working temperatures of the engine. The Carnot cycle goes in the cycle *ABCDA* with *AB* being an isothermal expansion. The volume at points *A* and *C* of the cycle are $5.0 \times 10^{-3}\ \text{m}^3$ and 0.15 L, respectively. The engine operates between two thermal baths of temperature 500 K and 300 K. (a) Find the values of volume at *B* and *D*. (b) How much heat is absorbed by the gas in the *AB* isothermal expansion? (c) How much work is done by the gas in the *AB* isothermal expansion? (d) How much heat is given up by the gas in the *CD* isothermal expansion? (e) How much work is done by the gas in the *CD* isothermal compression? (f) How much work is done by the gas in the *BC* adiabatic expansion? (g) How much work is done by the gas in the *DA* adiabatic compression? (h) Find the value of efficiency of the engine based on the net work and heat input. Compare this value to the efficiency of a Carnot engine based on the temperatures of the two baths.

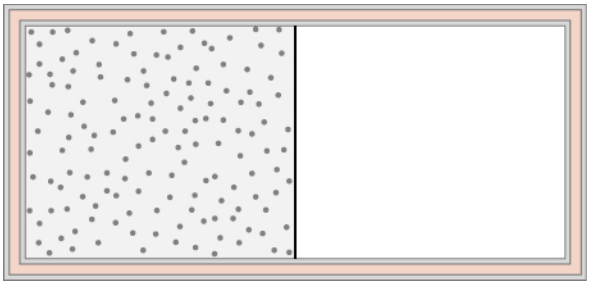
70. A 5.0-kg wood block starts with an initial speed of 8.0 m/s and slides across the floor until friction stops it. Estimate the resulting change in entropy of the universe. Assume that everything stays at a room temperature of $20\,°\text{C}$.

71. A system consisting of 20.0 mol of a monoatomic ideal gas is cooled at constant pressure from a volume of 50.0 L to 10.0 L. The initial temperature was 300 K. What is the change in entropy of the gas?

72. A glass beaker of mass 400 g contains 500 g of water at $27\,°\text{C}$. The beaker is heated reversibly so that the temperature of the beaker and water rise gradually to $57\,°\text{C}$. Find the change in entropy of the beaker and water together.

73. A Carnot engine operates between $550\,°\text{C}$ and $20\,°\text{C}$ baths and produces 300 kJ of energy in each cycle. Find the change in entropy of the (a) hot bath and (b) cold bath, in each Carnot cycle?

74. An ideal gas at temperature *T* is stored in the left half of an insulating container of volume *V* using a partition of negligible volume (see below). What is the entropy change per mole of the gas in each of the following cases? (a) The partition is suddenly removed and the gas quickly fills the entire container. (b) A tiny hole is punctured in the partition and after a long period, the gas reaches an equilibrium state such that there is no net flow through the hole. (c) The partition is moved very slowly and adiabatically all the way to the right wall so that the gas finally fills the entire container.



75. A 0.50-kg piece of aluminum at $250\,°\text{C}$ is dropped into 1.0 kg of water at $20\,°\text{C}$. After equilibrium is reached, what is the net entropy change of the system?

76. Suppose 20 g of ice at $0\,°\text{C}$ is added to 300 g of water at $60\,°\text{C}$. What is the total change in entropy of the mixture after it reaches thermal equilibrium?

77. A heat engine operates between two temperatures such that the working substance of the engine absorbs 5000 J of heat from the high-temperature bath and rejects 3000 J to the low-temperature bath. The rest of the energy is converted into mechanical energy of the turbine. Find (a) the amount of work produced by the engine and (b) the efficiency of the engine.

78. A thermal engine produces 4 MJ of electrical energy while operating between two thermal baths of different temperatures. The working substance of the engine rejects 5 MJ of heat to the cold temperature bath. What is the efficiency of the engine?

79. A coal power plant consumes 100,000 kg of coal per hour and produces 500 MW of power. If the heat of combustion of coal is 30 MJ/kg, what is the efficiency of the power plant?

80. A Carnot engine operates in a Carnot cycle between a heat source at $550\,°\text{C}$ and a heat sink at $20\,°\text{C}$. Find the efficiency of the Carnot engine.

81. A Carnot engine working between two heat baths of temperatures 600 K and 273 K completes each cycle in 5 sec. In each cycle, the engine absorbs 10 kJ of heat. Find the power of the engine.

82. A Carnot cycle working between $100\,°\text{C}$ and $30\,°\text{C}$ is used to drive a refrigerator between $-10\,°\text{C}$ and $30\,°\text{C}$. How much energy must the Carnot engine produce per second so that the refrigerator is able to discard 10 J of energy per second?

CHALLENGE PROBLEMS

83. (a) An infinitesimal amount of heat is added reversibly to a system. By combining the first and second laws, show that $dU = TdS - dW$. (b) When heat is added to an ideal gas, its temperature and volume change from T_1 and V_1 to T_2 and V_2. Show that the entropy change of *n* moles of the gas is given by

$$\Delta S = nC_v \ln\frac{T_2}{T_1} + nR \ln\frac{V_2}{V_1}.$$

84. Using the result of the preceding problem, show that for an ideal gas undergoing an adiabatic process, $TV^{\gamma - 1}$ is constant.

85. With the help of the two preceding problems, show that ΔS between states 1 and 2 of *n* moles an ideal gas is given by

$$\Delta S = nC_p \ln\frac{T_2}{T_1} - nR \ln\frac{p_2}{p_1}.$$

86. A cylinder contains 500 g of helium at 120 atm and $20\,°\text{C}$. The valve is leaky, and all the gas slowly escapes isothermally into the atmosphere. Use the results of the preceding problem to determine the resulting change in entropy of the universe.

87. A diatomic ideal gas is brought from an initial equilibrium state at $p_1 = 0.50\,\text{atm}$ and $T_1 = 300\,\text{K}$ to a final stage with $p_2 = 0.20\,\text{atm}$ and $T_1 = 500\,\text{K}.$ Use the results of the previous problem to determine the entropy change per mole of the gas.

88. The gasoline internal combustion engine operates in a cycle consisting of six parts. Four of these parts involve, among other things, friction, heat exchange through finite temperature differences, and accelerations of the piston; it is irreversible. Nevertheless, it is represented by the ideal reversible *Otto cycle*, which is illustrated below. The working substance of the cycle is assumed to be air. The six steps of the Otto cycle are as follows:

i. Isobaric intake stroke (*OA*). A mixture of gasoline and air is drawn into the combustion chamber at atmospheric pressure p_0 as the piston expands, increasing the volume of the cylinder from zero to V_A.

ii. Adiabatic compression stroke (*AB*). The temperature of the mixture rises as the piston compresses it adiabatically from a volume V_A to V_B.

iii. Ignition at constant volume (*BC*). The mixture is ignited by a spark. The combustion happens so fast that there is essentially no motion of the piston. During this process, the added heat Q_1 causes the pressure to increase from p_B to p_C at the constant volume $V_\text{B}(=V_\text{C})$.

iv. Adiabatic expansion (*CD*). The heated mixture of gasoline and air expands against the piston, increasing the volume from V_C to V_D. This is called the *power stroke*, as it is the part of the cycle that delivers most of the power to the crankshaft.

v. Constant-volume exhaust (*DA*). When the exhaust valve opens, some of the combustion products escape. There is almost no movement of the piston during this part of the cycle, so the volume remains constant at $V_A(=V_D)$. Most of the available energy is lost here, as represented by the heat exhaust Q_2.

vi. Isobaric compression (*AO*). The exhaust valve remains open, and the compression from V_A to zero drives out the remaining combustion products.

(a) Using (*i*) $e = W/Q_1$; (*ii*) $W = Q_1 - Q_2$; and (*iii*) $Q_1 = nC_v(T_C - T_B)$, $Q_2 = nC_v(T_D - T_A)$, show that

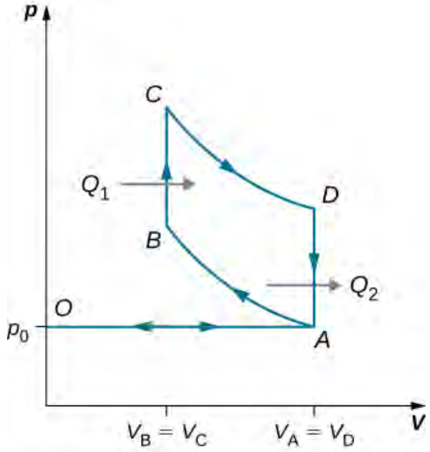
$$e = 1 - \frac{T_D - T_A}{T_C - T_B}.$$

(b) Use the fact that steps (ii) and (iv) are adiabatic to show that

$$e = 1 - \frac{1}{r^{\gamma - 1}},$$

where $r = V_A/V_B$. The quantity r is called the *compression ratio* of the engine.

(c) In practice, r is kept less than around 7. For larger values, the gasoline-air mixture is compressed to temperatures so high that it explodes before the finely timed spark is delivered. This *preignition* causes engine knock and loss of power. Show that for $r = 6$ and $\gamma = 1.4$ (the value for air), $e = 0.51$, or an efficiency of 51%. Because of the many irreversible processes, an actual internal combustion engine has an efficiency much less than this ideal value. A typical efficiency for a tuned engine is about 25% to 30%.



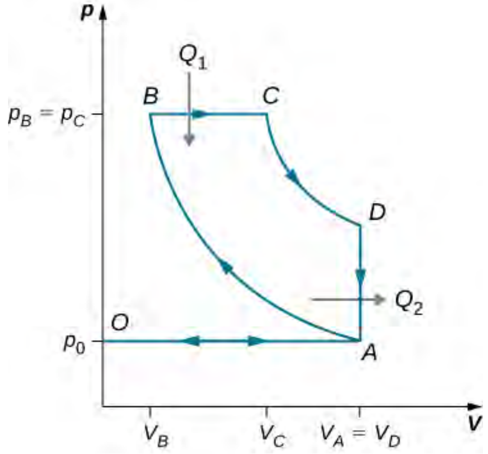
89. An ideal *diesel* cycle is shown below. This cycle consists of five strokes. In this case, only air is drawn into the chamber during the intake stroke *OA*. The air is then compressed adiabatically from state *A* to state *B*, raising its temperature high enough so that when fuel is added during the power stroke *BC*, it ignites. After ignition ends at *C*, there is a further adiabatic power stroke *CD*. Finally, there is an exhaust at constant volume as the pressure drops from p_D to p_A, followed by a further exhaust when the piston compresses the chamber volume to zero.

(a) Use $W = Q_1 - Q_2$, $Q_1 = nC_p(T_C - T_B)$, and $Q_2 = nC_v(T_D - T_A)$ to show that $e = \frac{W}{Q_1} = 1 - \frac{T_D - T_A}{\gamma(T_C - T_B)}$.

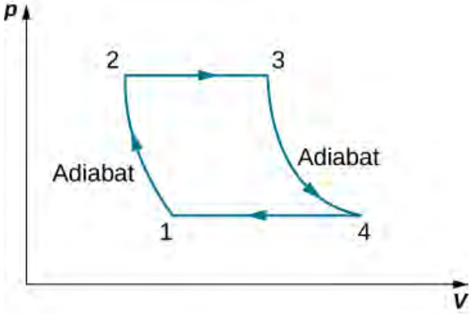
(b) Use the fact that $A \to B$ and $C \to D$ are adiabatic to show that

$$e = 1 - \frac{1}{\gamma}\frac{\left(\frac{V_C}{V_D}\right)^{\gamma} - \left(\frac{V_B}{V_A}\right)^{\gamma}}{\left(\frac{V_C}{V_D}\right) - \left(\frac{V_B}{V_A}\right)}.$$

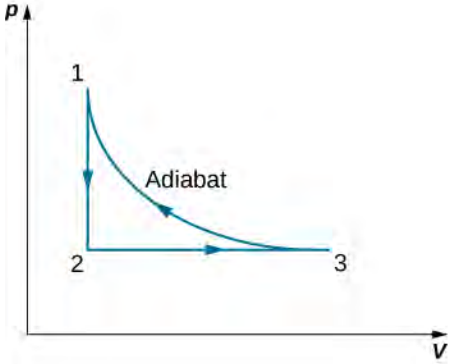
(c) Since there is no preignition (remember, the chamber does not contain any fuel during the compression), the compression ratio can be larger than that for a gasoline engine. Typically, $V_A/V_B = 15$ and $V_D/V_C = 5$. For these values and $\gamma = 1.4$, show that $\varepsilon = 0.56$, or an efficiency of 56%. Diesel engines actually operate at an efficiency of about 30% to 35% compared with 25% to 30% for gasoline engines.



90. Consider an ideal gas Joule cycle, also called the Brayton cycle, shown below. Find the formula for efficiency of the engine using this cycle in terms of P_1, P_2, and γ.



91. Derive a formula for the coefficient of performance of a refrigerator using an ideal gas as a working substance operating in the cycle shown below in terms of the properties of the three states labeled 1, 2, and 3.



92. Two moles of nitrogen gas, with $\gamma = 7/5$ for ideal diatomic gases, occupies a volume of $10^{-2}\,\mathrm{m}^3$ in an insulated cylinder at temperature 300 K. The gas is adiabatically and reversibly compressed to a volume of 5 L. The piston of the cylinder is locked in its place, and the insulation around the cylinder is removed. The heat-conducting cylinder is then placed in a 300-K bath. Heat from the compressed gas leaves the gas, and the temperature of the gas becomes 300 K again. The gas is then slowly expanded at the fixed temperature 300 K until the volume of the gas becomes $10^{-2}\,\text{m}^3$, thus making a complete cycle for the gas. For the entire cycle, calculate (a) the work done by the gas, (b) the heat into or out of the gas, (c) the change in the internal energy of the gas, and (d) the change in entropy of the gas.

93. A Carnot refrigerator, working between $0\,°\text{C}$ and $30\,°\text{C}$ is used to cool a bucket of water containing $10^{-2}\ \text{m}^3$ of water at $30\,°\text{C}$ to $5\,°\text{C}$ in 2 hours. Find the total amount of work needed.